Tutorial
Room Hall 3A - Session TS-SuA

Tutorial and Perspective Session (Invitation Only)
Moderators: **Markku Leskelä**, University of Helsinki, Finland, **Mikko Ritala**, University of Helsinki, **Fred Roozeboom**, University of Twente and Carbyon B.V., The Netherlands, **Dmitry Suyatin**, AlixLabs A.B.

1:00pm TS-SuA-1 Thermal Atomic Layer Deposition of Electropositive Metal and Element Films and Assessment of Inherently Selective Growth on Substrates, *Charles Winter,* Wayne State University **INVITED**
Our laboratory is developing new chemical precursors for the growth of electropositive metal and element thin films by atomic layer deposition (ALD). We are also interested in processes that exhibit area selective growth, especially inherently selective growth where no blocking or deactivating groups are required. ALD has many current applications in copper metallization, diffusion barriers, liners, and transistor fabrication. Thermal ALD is often preferred because plasmas can afford low conformal coverage due to radical recombination on the walls of deep and narrow features.There has been extensive progress in the thermal ALD of copper and noble metal films in recent years, because the positive electrochemical potentials allow relatively easy reduction of precursor ions to the metals. Thermal ALD approaches to most other metals and elements in the periodic table are not well developed, due to the negative electrochemical potentials of the ions and a current lack of ALD co-reagents that can convert the ions to the metals or elements. In this tutorial, the thermal ALD growth of electropositive metals such as nickel, cobalt, aluminum, and others will be described. The ALD of nickel and cobalt metal films has been achieved using precursors containing diazadienyl (RN=CHCH=NR) ligands. These precursors enable the deposition of cobalt and nickel metal films at temperatures below 200 °C and use alkylamines as benign co-reagents. Growth rates are high (0.60 Å/cycle for nickel, 0.98 Å/cycle for cobalt), high purity, low resistivity metal films are obtained, and the films have low rms roughnesses. The processes exhibit inherent selective growth on metal substrates such as platinum, ruthenium, and copper. By contrast, no growth is observed on insulating substrates. We will also describe a new family of thermal ALD precursors and processes to cobalt and copper metal films. Inherently selective growth of cobalt and copper on metal substrates is obtained with appropriate co-reactants. Finally, a thermal ALD process for the growth of aluminum metal films will be presented. This process entails treatment of surface-bound $AlCl_3$ with a thermally stable, volatile aluminum hydride co-reagent. The growth rate for the aluminum metal ALD process is high, and high purity, low resistivity aluminum metal films are obtained. Prospects for the area selective growth of aluminum metal films will be presented. These examples demonstrate that thermal ALD processes can be enabled for electropositive metals through careful design of precursors and chemistry.

1:45pm TS-SuA-4 Area Selective Atomic Layer Deposition: What, What for, and What Next?, *Stacey Bent,* Stanford University **INVITED**
This tutorial on area selective atomic layer deposition (AS-ALD) will explain what it is, what it is useful for, and what is coming next. We will discuss why AS-ALD has become an active area of research and development as an additive process for achieving pattern features at the ~10 nm length scale for semiconductor applications, as well as for new applications within fields as diverse as catalysis and optoelectronics. We will cover what AS-ALD is and the fundamental concepts behind deposition selectivity and how selectivity is quantified. The tutorial will provide a description of different strategies to achieve AS-ALD, including the use of both large and small molecule inhibitors, the role of molecular tuning in achieving selectivity, and methods for improving selectivity. These approaches will be illustrated with representative examples of AS-ALD. Finally, we will look to what is next, including recent developments and a discussion of emerging challenges and opportunities for AS-ALD.

2:30pm TS-SuA-7 Atomic Layer Etching: Basics, New Developments & Applications, *Thorsten Lill,* Clarycon Nanotechnology Research, Inc.**INVITED**
Atomic layer etching (ALE) is becoming an important technology for patterning and shaping of electronic and photonic devices. This tutorial briefly recaps the fundamentals of thermal, directional and plasma assisted atomic layer etching. Performance benefits and limitations for ALE in comparison to the continuous processing analogues such as reactive ion etching, radical and vapor etching are the consequence of the cyclic self-limited structure of ALE processes. This section will conclude with a list of selection criteria for the appropriate etching technology for a given task.

In the second part of the tutorial the enormous progress in the development of new ALE process and chemistries will be illustrated using published and potential practical applications in the manufacturing of electronic and photonics devices. They include multi-patterning, advanced planar and 3D logic and memory devices, 2D materials, emerging memories comprised of hard to etch materials, power and optical devices and combinations of ALE and atomic layer deposition.

3:30pm TS-SuA-11 Thin Film Process Technologies for the Atomic Scale Era, *Robert Clark,* TEL **INVITED**
Continued device density scaling according to Moore's Law has resulted in the adoption of 3D devices and architectures, and driven critical dimensions down to atomic scales. This tutorial briefly reviews the trends in device scaling since Dennard-style linear shrinking became untenable and outlines the forces driving 3D integration going forward as well as the new challenges these changes pose for future manufacturing process technologies. A look forward at the expected evolution of integrated circuit manufacturing through 3D monolithic and heterogeneous integration is presented to frame the future opportunities and challenges for advanced process technologies. The seminar then introduces selective, self-limited and atomic scale thin film process technologies that can enable 3 nm and beyond semiconductor manufacturing including plasma and thermal chemical vapor deposition (CVD), atomic layer deposition (ALD) and atomic layer etching (ALE) technologies. Selective processing including area selective deposition (ASD) is explained as an emerging technology enabling new device nodes, integration schemes and eventually the shift toward new patterning paradigms. The scope of the discussion includes examples of how these technologies enable self-aligned and sub-lithographic patterning and integration of new device and interconnect structures suitable for atomic scale process nodes. Finally, a path forward for thin film process technology evolution is postulated by summarizing the major trends that will drive thin film innovation in semiconductor manufacturing over the next decade and beyond.

4:15pm TS-SuA-14 ALD for PV, Current State and Future Prospects, *Wei-Min Li,* Jiangsu Leadmicro Nano Technology Co. Ltd., China **INVITED**
Silicon based solar cells is rapidly expanding its market share in global clean energy sector. During past few years, industrial ALD has played an instrumental role for increasing conversion efficiency and significantly reducing the manufacturing cost of solar cells, that enabled quest for grid parity. Today, hundreds of GW ALD enabled PV modules are in operation either in power plants or on roof tops worldwide.

Driven by rapid technology transformation from PV industry, both ALD and PEALD are now well recognized in solar cell production lines not only for replacing traditional PVD, CVD for PERC/PERL/PERT cell manufacturers, but also for pioneering alternative solutions for next generation TOPCon, IBC, HJT, as well as tandem solar cell technology. Batch type ALD and PEALD reactors are widely used for the critical layers for silicon-based cell manufacturing. ALD enabled novel n-TOPCon solar cells have reached a conversion efficiency of above 25.5% in production with record throughput at well over 20000 wafers per hour. At mean time, rapid progress of novel materials, for example perovskite for solar cell is providing new opportunities for ALD innovation for PV industry. In-line ALD that can handle 1,2x2.4m glass sheet is entering pilot production line for critical applications. With continuous improvement of materials and process integration, ALD technology is expected to play even an wider role in PV industry.

5:00pm TS-SuA-17 Sustainable Atomic Layer Processing for Semiconductor Applications, *Job Soethoudt,* IMEC, Belgium **INVITED**
Research into atomic layer processing is key to meeting the growing demand for increasingly complex and versatile semiconductor applications. However, the detrimental adverse sustainability impacts of these semiconductor applications need to be addressed to render them viable for the future. A large part of the life cycle impacts of semiconductor products comes from manufacturing, and recently increasing research efforts are dedicated to making manufacturing more sustainable. The figure below illustrates the CO_2-equivalent emissions for production of an integrated circuit, highlighting the contribution of deposition and etch steps. Understanding the source of these contributions can be a catalyst for developing new atomic layer etch and deposition processes with sustainability in mind.

Through data provided within the imec.netzero platform (of which a version is publicly available online) we find that opportunities for sustainable atomic layer processing are as diverse as the field itself, touching on

precursor design, reaction kinetics, and surface modification, as well as process engineering and hardware improvements. Moreover, in some cases the unique control offered by atomic layer processing can itself unlock greener IC chip manufacturing methods by unlocking new integration pathways yielding simplified process flows. Together, these opportunities provide new avenues for research to enable a future of sustainable atomic layer deposition and etch processes.

Sunday Evening, August 4, 2024

Atomic Layer Etching

Room Hall 3 - Session ALE-SuP

Atomic Layer Etching Poster Session

ALE-SuP-1 Removing Defects from InGaP Surfaces Using Thermal Atomic Layer Etching (ALE), *R. Edel, Andrew Cavanagh, T. Nam, S. George,* University of Colorado Boulder

Indium gallium phosphide (InGaP) is widely used for red light-emitting diode (LED) devices. Surface defects on LED devices can lead to non-radiative electron/hole pair recombination that reduces their light output. This light quenching effect is more severe for smaller LED devices that have high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species from plasma processing used to fabricate the LEDs. Thermal ALE may provide a method to remove these surface defects.

Thermal InGaP ALE was performed using static, sequential hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) exposures. This procedure yields etch rates of 0.5–1.0 Å/cycle at temperatures from 300–330 °C, respectively. Etching with only HF/DMAC exposures often produced a chemically distinct top layer due to a conversion mechanism. This conversion could be avoided by first removing the InGaP native oxide using sequential HF and trimethylaluminum (TMA) exposures. This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy. This apparatus allows the sample to be characterized throughout the thermal ALE process without exposure to air.

The removal of surface defects by ALE was studied using *ex situ* X-ray photoelectron spectroscopy (XPS). InGaP samples damaged by Ar^+ ion sputtering were analyzed before and after thermal ALE by tracking the shifted components in the P 2p XPS region that correspond to damage from sputtering. An XPS scan of an unsputtered InGaP sample shows only a bulk doublet (Figure 1a). An InGaP sample after sputtering displays two additional shifted components that correspond to undercoordinated atoms in the damaged lattice (Figure 1b).

InGaP ALE can then remove the XPS features associated with the damaged lattice. A bulk-like XPS spectrum showing minimal damage was recovered after 50 ALE cycles for a sample initially exposed to 500 eV sputtering (Figure 2a). By contrast, annealing for 72 hours at 300 C without etching was not sufficient to eliminate the damage. AES analysis similarly showed that the argon implanted in the sample by sputtering was removed after etching but not annealing. Increasing the sputtering ion energy to 2 keV required more extensive etching to remove the sputter damage. With the higher ion energy of 2 keV, 100 ALE cycles were able to largely remove the surface defects (Figure 2b). The etch depth consistent with 100 ALE cycles indicates a damaged material depth of ~4-5 nm.

ALE-SuP-2 Tailored Waveforms for CCP Discharges in ALE Applications, *Anna Nelson, S. Mohr,* Quantemol Ltd., UK

Atomic layer etching (ALE) is increasingly used in the manufacturing of semiconductor tools as they give more control over the resulting etching profiles than traditional etching techniques. While different approaches to ALE exist, many of them employ plasmas in one or more steps of the ALE process, be it to use the neutral radicals produced in the plasma to alter the surface or the ions to remove the altered top layer [1].

For such applications, independent control of ion flux and ion energy is highly desirable. Single frequency capacitively coupled discharges (CCPs) do not offer this, as the input power affects both flux and energy. Dual frequency discharges allow this to some extent, but it is limited due to, for example, increased ionization by secondary electrons at high powers of the low frequency. Furthermore, traditional CCPs usually produce bimodal ion energy distribution functions which can cover several 10s to 100s of eV with sharp peaks at either end, so the ion energy cannot be easily limited to a small interval of energies, which is desirable especially for ALE applications, so that the ions remove the top layer of the surface but do not damage the underlying bulk [1].

An alternative approach to achieve this desired control are tailored waveforms. These can range from so-called asymmetric waveforms combining a fundamental frequency with even multiples [2] to non-sinusoidal waveforms typically consisting of sharp voltage peaks [1] followed by a relatively long interval of an almost constant voltage. While it has been demonstrated that these type of CCPs offer independent control of ion flux and energy and/or are able to limit the ion energy to narrow energy intervals, they have not yet been well studied in industrial applications.

This presentation will show first efforts to simulate industrial applications of tailored waveform CCPs using the well-established 2D plasma simulation code HPEM [3]. The simulations are carried out in gases used in typical ALE applications such as chlorine containing molecules whereas most investigations so far were limited to rare gases such as argon which give principle insight into the effects taking place in such discharges are of limited use to understand and optimize industrial processes. We will demonstrate first results from these simulations.

[1] T. Faraz et al. J. Appl. Phys. 128 213301 (2020)
[2] U Czarnetzki et al Plasma Sources Sci. Technol. 20 024010 (2011)
[3] M. Kushner J. Phys. D 42 194013 (2009)

ALE-SuP-3 Atomic Layer Control of 2D WS₂ Through the Formation of Volatile Tungsten Oxychloride, *Hye Won Han, J. Kang, J. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

Transition metal dichalcogenides (TMDs) are two-dimensional materials renowned for their variable electronic and optoelectronic properties depending on the thickness of the materials. Precise layer control of two-dimensional TMDs is crucial for their integration into advanced material and device applications, necessitating a refined etching technique. Previous research approaches to layer control using radical adsorption and ion desorption processes, which can cause physical damage. To address these challenges, we introduce the layer control of WS_2 with the formation of volatile tungsten oxychloride designed for the sequential removal of WS_2 layers. Oxychloride is formed on the WS_2 surface using an ALE-based cyclic sequential process and the volatile tungsten oxychloride can be removed by heating. Utilizing a radical-only mechanism, we can ensure damage-free and isotropic etching, which is essential for three-dimensional device fabrication. By offering the layer control of WS_2, this research opens new avenues for the integration of TMDs into future material and device technologies, marking a significant advancement in the field of advanced materials research.

ALE-SuP-4 Thermal Atomic Layer Etching of Ternary Indium Gallium Phosphide Based on Fluorination and Ligand-Exchange Reactions, *TAEWOOK NAM, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) has been developed for metal oxides (Al_2O_3, HfO_2, ZrO_2, ZnO, WO_3, SiO_2), nitrides (SiN, TiN, AlN), elements (Ni, Co, Mo, Si, W), and sulfides (ZnS). This study introduces the thermal ALE of a ternary phosphide material – indium gallium phosphide (InGaP). The InGaP films were grown on GaAs (100) substrate using metal organic chemical vapor deposition (MOCVD). The thickness of the InGaP films was monitored during thermal ALE by spectroscopic ellipsometry (SE). InGaP ALE was first demonstrated using hydrofluoric acid (HF) and dimethylaluminum chloride (DMAC). HF and DMAC exposures under viscous flow conditions did not etch InGaP. However, with static 100 mTorr and 1 Torr exposures of HF and DMAC, respectively, InGaP was etched at 0.6 Å/cycle after a short etch delay. The etching delay is presumably caused by native oxide on the InGaP surface. At 200 °C, the etch rates were 0.05, 0.15, 0.41, 0.6, and 1.12 Å/cycle, at 225, 250, 275, 300, and 325 °C, respectively. After ALE, Auger electron spectroscopy (AES) detected Al on the InGaP surface. The Al AES signal indicates there could be a conversion reaction between the DMAC precursor and InGaP. Another etching chemistry was also developed for InGaP ALE using xenon difluoride (XeF_2) and boron trichloride (BCl_3). These precursors increased the etch rate and decreased the etching temperature compared with HF and DMAC. At XeF_2 and BCl_3 pressures of 20 and 230 mTorr, InGaP ALE showed linear thickness decrease versus ALE cycles after a short etch delay. When the XeF_2 and BCl_3 dose times were 1.5 and 1 s, respectively, the etch rate of InGaP at 200 °C was 2.2 Å/cycle. The etch rate saturation versus precursor dose times was also characterized at 175 °C. The etch rate was saturated at 2.5 Å/cycle when the XeF_2 and BCl_3 dose times were ≥ 1.5 and ≥1 s, respectively. The larger etch rates and lower etching temperatures using XeF_2 are attributed to more favorable fluorination with XeF_2. From thermochemical calculations, fluorination of InP and GaP using HF at 200 °C has standard Gibbs Free Energies of DG° = -39 and -26 kcal/mol. In contrast, fluorination using XeF_2 has much larger standard Gibbs Free Energies of DG° = -424 and -411 kcal/mol, respectively.

ALE-SuP-5 Spontaneous Etching of Group V and VI Metal Oxides by Deoxychlorination Using Thionyl Chloride, *Troy Colleran, S. George,* University of Colorado at Boulder

Group V and VI metals and their respective oxides are of interest in microelectronic, electrochemical and sensing devices. Thermal etching of these materials provides a method to fabricate and clean these devices. The spontaneous etching of Group V and VI metal oxides was studied using

an apparatus equipped with a quadrupole mass spectrometer (QMS). The QMS could measure the volatile etch products produced during thionyl chloride (SOCl₂) exposure to nanopowders of Group V and VI metal oxides. Spontaneous thermal etching of MoO_3, WO_3, WO_2, VO_2, V_2O_5, and Nb_2O_5 was observed during SOCl₂ exposures at 200℃. Etching was monitored by the presence of volatile metal oxychlorides during SOCl₂ exposures in combination with the measured mass losses of the nanopowder after SOCl₂ exposures. No etching was detected on MoO_2 or Cr_2O_3. The volatile etch products were different dependent on the oxidation state of the metal center in the metal oxide. Species in the form of MO_2Cl_2 were most common for metals in the +6 oxidation state, such as MoO_3 or WO_3. Exclusively $MOCl_3$ species were observed from metals in the +5 oxidation state. Lower oxidation states acted as a barrier as illustrated by the inability of MoO_2 and Cr_2O_3 to undergo spontaneous etching. However, in the case of WO_2 and VO_2, SOCl₂ was able to perform as an oxidizing agent and produced WO_2Cl_2 and $VOCl_3$ etching products, respectively. The ability to spontaneously etch these metal oxides provides a method for cleaning the native oxides from pure Group V and VI metal films. In addition, combined with an oxidation step, the spontaneous etching of these metal oxides provides a pathway for metal ALE.

ALE-SuP-6 Phase Transition of Molybdenum Disulfide by Controlled Ion Beam ALE Method, *Ji Eun Kang*, H. Han, J. Kim, G. Yeom, Sungkyunkwan University (SKKU), Republic of Korea

Among the two-dimensional transition-metal dichalcogenides (TMDs), molybdenum disulfide (MoS_2) exhibits promising capabilities for advanced electronic and optoelectronic devices. However, the performance of these devices is often hindered by the Schottky barrier and contact resistance issues arising from the interface between TMD materials and metal electrodes. To address this challenge, various techniques such as alignment of metal work functions, lithium intercalation, application of strain, and colloidal synthesis have been explored. Despite their potential, achieving uniform application of these techniques across large areas remains as a challenge. A novel strategy employing defect engineering to facilitate a phase transition from the 2H to the 1T phase has emerged to reduce contact resistance. But time-dependent processes and uncontrolled energy sources in these methods makes it difficult to uniformly create chalcogen defects in TMDs, potentially compromising the quality of the 1T phase. In this study, a self-limiting technique used for MoS_2 ALE that precisely employs controlled Ar ion beams was investigated to selectively remove the top sulfur layer of MoS_2, ensuring a uniform metal transition (MT) of MoS_2 with a defined threshold ion energy. Furthermore, the conversion from the 1T phase back to the p-type branch was investigated through the incorporation of nitrogen atoms at the sites of removed sulfur, offering a novel approach to enhance the electronic properties of MoS_2.

ALE-SuP-8 Ab Initio Investigation of Chelation on Amorphous CoCl₂ Films for Atomic Layer Etching, *Eugene Huh*, S. Lee, Ewha Womans University, Republic of Korea

A thermal atomic layer etching process for Cobalt (Co) has been developed using Chlorination with BCl₃ and Chelation with Hexafluoroacetylacetone (Hhfac). A thermal atomic layer etching process for Cobalt (Co) has been developed using Chlorination with BCl₃ and Chelation with Hexafluoroacetylacetone (Hhfac). A previous computational study focused on DFT research about the chelation of adsorption and desorption of Hhfac, using the $CoCl_2$ flakes model, as the coordination with Cl atoms proceeds through the termination of Co atoms on the amorphous surfaces. It was confirmed that the chlorination process is most stable when four Cl atoms form a coordination bond with Co, and the chelation process is most stable when CoCl2hfac and HCl are formed and then removed. Additionally, it was revealed that the adsorption of Hhfac during the chelation process is the rate-determining step.

In this study, we investigate the processes of chlorination and chelation with Hhfac on amorphous Co surfaces by performing DFT calculations. To this end, we perform the Monte Carlo simulations and Ab initio Molecular Dynamics (AIMD) to generate the various amorphous Co structures. Subsequently, we performed DFT calculations to obtain thermodynamic information about the chlorination of amorphous Co according to the Cl atom ratio and chelation process through coordination with Hhfac. On the amorphous $CoCl_2$ surface, it was observed that structures with low coordination numbers, similar to the $CoCl_2$ disk model, are energetically stable. Unlike in the disk model, it was identified that Co-Co bonding influences these structures. Such computational results enhance our understanding of atomic layer etching in experimentally obtained amorphous Co structures.

References [1] Kim, Y., Chae, S., Ha, H., Lee, H., Lee, S., & Chae, H. (2023). Thermal atomic layer etching of cobalt using plasma chlorination and chelation with hexafluoroacetylacetone. Applied Surface Science, 619, 156751.

ALE-SuP-9 Selective Isotropic Atomic Layer Etching of Silicon Nitride over Silicon Oxide with Surface Fluorination using CF₄/H₂O Plasma and Heating, *Daeun Hong*, H. Lee, M. Jeon, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea

In this work, highly selective isotropic atomic layer etching (ALE) process was developed for Si_3N_4 over SiO_2 by forming ammonium fluorosilicate (AFS) using CF₄/H₂O plasma and by removing the modified layer with heating. The AFS layer was selectively formed on Si_3N_4 surface with CF₄/H₂O plasma in the modification step, and the AFS layer was decomposed by heating in the removal step. The effect of the CF₄/H₂O gas ratio on the AFS formation was investigated in the modification step. The AFS layer was formed on Si_3N_4 over a wide range of H₂O/ (CF₄+H₂O) ratios from 46 % to 82%, but the layer was partially removed into NH_3, SiF_4, and HCN with excessive H radicals at the H₂O/ (CF₄+H₂O) ratios of 75% and above. The removal characteristic of AFS was investigated depending on the heating temperature in the removal step. The AFS was totally decomposed at a temperature of 200 ℃ or higher. The infinite etch rate selectivity of Si_3N_4 over SiO_2 was achieved at the H₂O/ (CF₄+H₂O) ratios above 70%. The high selectivity was attributed to the decrease in F radicals as the H₂O flow rate increases by preventing spontaneous etching of SiO_2 at the high H₂O ratio. Etch per cycle of Si_3N_4 was saturated to 7 nm/cycle after 20 min of AFS formation time with H₂O/ (CF₄+H₂O) ratio of 70%. No carbon residues were observed on the Si_3N_4 surface after the ALE process with CF₄/H₂O plasma.

ALE-SuP-10 Selective Thermal Atomic Layer Etching of Molybdenum & Other Metals for Semiconductor Metallization, *M. McBriarty, N. Vu, Bhushan Zope*, Merck KGaA, Darmstadt, Germany

Performance of semiconductor integrated devices continues to be limited by metallization scaling. Molybdenum will play a key role in device scaling and is being evaluated for applications in logic interconnect, 3D-NAND word-line, and DRAM word-line. Mo enables low resistivity films while also eliminating the need for high-resistivity barriers, further accentuating its resistivity benefit to the metallization stack.

Selective thermal atomic layer etching (ALE) of molybdenum is critical for the successful integration of molybdenum metal in integrated device manufacturing. We have identified thermal ALE methods to selectively etch Mo metal without etching dielectric (SiO2) or semiconductor (Si) films. Mo etch is achieved by either oxidizing or chlorinating the Mo surface, followed by thermochemical volatilization of Mo complexes. Surface-limited reactions provide Mo etching without compromising its resistivity and enable consistent etch in high aspect ratio features. Surface quality is preserved, indicated by minimal surface roughening or contamination.

By demonstrating multiple pathways for Mo thermal ALE, we enable manufacturers to choose an ALE process that is suitable for a given device integration. We also extend these thermal ALE methods to other metals of interest, including Co, W, and TiN.

ALE-SuP-11 Theoretical investigation on Plasma Decomposition and Recombination Reaction Characteristics of C₄F₈O Isomers as Alternatives to HFC, *Mihyeon Jo*, S. Lee, Ewha Womans University, Republic of Korea

As we progress towards a carbon-neutral society, there is a growing emphasis on utilizing semiconductor etching gases with reduced global warming potentials. This necessitates the exploration of alternative gases to replace conventional perfluorinated compounds (PFCs) currently employed in industrial processes. Oxygen-containing fluorocarbons have emerged as promising candidates for this role due to their lower propensity to generate environmental pollutants such as CO, CO2, and COF2. In this context, the potential utilization of compounds like Perfluoro-2-butanone and Perfluorotetrahydrofuran in ion plasma etching processes is of particular interest. These compounds offer the possibility of maintaining high process efficiency while minimizing environmental impact.

In this study, we theoretically investigate and compare the decomposition and recombination characteristics of the three isomers of C_4F_8O: Fluoro-ketone derivatives, Perfluoro-2-butanone, and Fluoro-epoxide derivatives, perfluoroisobutylene oxide, as well as the ring compound

Perfluorotetrahydrofuran, using the Gaussian 16 software program. Additionally, our study aims to provide comprehensive insights into the decomposition and recombination pathways of neutral molecules, as well as ionization-induced decomposition pathways. By examining these aspects, we seek to offer a thorough understanding of the chemical transformations occurring during the decomposition and recombination processes of the investigated Fluoro-ketone and Fluoro-epoxide derivatives, as well as Perfluorotetrahydrofuran. This holistic approach allows for a detailed analysis of both neutral-state and ionization-induced reactions, shedding light on the intricate mechanisms governing the behavior of these compounds in plasma environments commonly encountered in semiconductor fabrication processes. Through elucidating the various reaction pathways, our research endeavors to inform the design and optimization of gas precursors, ultimately facilitating the development of more efficient and environmentally sustainable semiconductor manufacturing technologies.

ALE-SuP-12 Plasma-Enhanced Atomic Layer Etching of Aluminum Oxide Using Trimethylaluminium and Nitrogen Trifluoride, *Ole Bieg*, *M. Kraut, T. Mikolajick,* Technische Universität Dresden, Institute of Semiconductors and Microsystems, Germany

While thermal atomic layer etching (ALE) processes using hydrogen fluoride (HF) and trimethylaluminum (TMA) have already been investigated [1][2], the critical nature of HF necessitates the explorations of alternative approaches. In this work, nitrogen trifluoride plasma (NF_3) is proposed as a replacement, offering improved handling characteristics as well as enhanced fluorination while maintaining the precision inherent in an ALE process. The investigation focuses on plasma-enhanced atomic layer etching (PEALE) of aluminum oxide (Al_2O_3) using NF_3 plasma and TMA.

This ALE process involves the fluorination of the Al_2O_3 surface by NF_3 plasma in the initial step, followed by the removal of the modified layer through a ligand exchange reaction in the second step using TMA. Experimental studies were conducted at temperatures ranging from 200°C to 300 °C, with a critical transition temperature observed at 250 °C, distinguishing between ALE of Al_2O_3 at high temperatures and atomic layer deposition (ALD) of AlF_3 at lower temperatures. The film growth at 200 °C indicates a shift in reaction mechanisms as a function of temperature.

The etch per cycle (EPC) showed a temperature-dependent saturation during TMA dosing and NF_3 plasma exposure. Etching of Al_2O_3 films was investigated with in–situ quartz crystal microbalance (QCM) measurements, a non-destructive measurement method for fast and accurate recording of saturation curves, which provides valuable insights into etching dynamics and process kinetics. In addition, an EPC of 1.4 Å/cyc was determined by in–situ spectroscopic ellipsometry (SE). The composition of the fluorinated Al_2O_3 layers as well as the composition after the removal step using TMA was determined using in–vacuo X-ray photoelectron spectroscopy (XPS).

Sources:

[1] S. M. George and Y. Lee, Prospects for Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions, *ACS Nano*, 10, 5, 4889–4894, 2016, doi: 10.1021/acsnano.6b02991.

[2] J. Reif, M. Knaut, S. Killge, M. Albert, T. Mikolajick, and J. W. Bartha, In situ studies on atomic layer etching of aluminum oxide using sequential reactions with trimethylaluminum and hydrogen fluoride, *Journal of Vacuum Science & Technology A*, 40, 3, 032602, 2022, doi: 10.1116/6.0001630

ALE-SuP-13 A Theoretical Study of Low Gwp Fluoro Gas Decomposition Properties, *Minji Kim, S. Lee,* Ewha Woman's University, Republic of Korea

Global warming is one of the serious problems about the earth's environment and the biggest cause of global warming is CO_2 released into the atmosphere, which has increased in concentration in proportion to the development of the industry, but other greenhouse gases such as perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have also been shown to have a much stronger greenhouse effect than carbon dioxide. [1]

Because hydrofluorocarbons (HFCs) have a high infrared absorbency and long atmospheric lifetimes. The Global Warming Potentials (GWPs) which shows the degree to which other greenhouse gases contribute to global warming based on the impact of carbon dioxide on global warming, is 1,000 to 10,000 times as high as that of CO_2 (whose GWP is 1). CHF_3 molecule which is the simplest molecule among HFCs gases has 11,700 GWP index. [1]

These HFCs gases are used in various device-fabrication processes in the semiconductor industry, CHF_3 is used in the etching process of SiO_2 films. Since semiconductors are an indispensable part of modern technology. it is time to discover alternative gases with a low GWP index that can be used in the etching process.

Therefore C_3F_6O, one of the several Precursor gas candidates of fluoro-ketone, will be investigated for several radical species that decomposed during the etching process compared to the reference etching gas CHF_3, and will be calculation the energy of decomposition path by performing computation details of the quantum chemical calculations, Gaussian09 and density-functional theory (DFT) using the Vienna ab initio simulation package (VASP). [2]

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ALE-SuP-14 Enhancing Doping Efficiency in 2D Semiconductors using Cyclic Doping Method, *Ji Min Kim, J. Kang, H. Han, G. Yeom,* Sungkyunkwan University, Republic of Korea

Two-dimensional (2D) semiconductors, characterized by their thickness-dependent electrical and optical properties, are emerging as promising materials for future semiconductor technologies. The quest for improved properties in 2D materials involves strategies such as precise thickness management, large-scale production, and effective doping strategies. Doping, in particular, is essential for modulating the electrical behavior of 2D semiconductors, but conventional methods like ion implantation pose challenges, including potential damage to the delicate structures of nanometer-thick layers. In response, alternative surface treatment techniques such as plasma-based radical adsorption, liquid solution spin coating, and immersion have been explored. Nonetheless, these approaches, which predominantly modify the surface, tend to be less effective as the material's thickness increases. Addressing the need for better vertical doping uniformity, this research presents a novel cyclic doping technique using a layer transfer process. This method improves the efficiency of doping across multiple layers and preserves the distinct layered structure of MoS_2. The development of this cyclic doping strategy promises to overcome current limitations in doping efficiency and uniformity, marking a significant advancement in the manipulation of 2D materials for semiconductor applications with atomic layer precision.

ALE-SuP-15 Repairing Defects in Organosilane Self-Assembled Monolayers, *Yasuharu Miyamoto, Y. Yoshida,* SCREEN Holdings Co., Ltd., Japan*; T. Utsunomiya,* Kyoto University, Japan*; K. Sawada, S. Kunieda, Y. Ueda,* SCREEN Holdings Co., Ltd., Japan*; H. Sugimura,* Kyoto University, Japan

Area selective atomic layer deposition has been extensively investigated for advanced semiconductor device fabrication. Self-assembled monolayers (SAMs) are used as a protective layer for selective film deposition, and therefore, a defect-free monolayer is crucial for achieving high selectivity. Missing and misaligned precursor molecules can cause defects in SAMs [1]. Defect-free monolayers can be created by repairing defects, that is, removing the misaligned precursor molecules so-called physisorbed molecules, adding chemisorption sites on the surface and SAM reformation.

In this study, we assembled octadecyltrichlorosilane (ODTS) SAMs onto a SiO_2 substrate and applied intermediate wet cleaning solutions between multiple SAM formation processes. The wet cleaning solutions were selected from among various solvents with different values of the Hansen solubility parameter (HSP) to remove the physisorbed SAM's precursor molecules. We assumed that solvents with an HSP value closer to that of ODTS exhibits better solubility and removability of the physisorbed ODTS molecules. The SC-1 solution (ammonia and hydrogen peroxide mixture) widely used for the wet cleaning process to remove organic residue and to oxidize the surface was selected for adding functional groups on the surface of the defect area. The defects were analyzed using methods that combined post etching and AFM observation [2].

SAM formation with no intermediate wet cleaning, 1,3-bis(trifluoromethyl) benzene (high solubility of ODTS) and decane (low solubility of ODTS) resulted in 43.7 and 32.1 and 19.6 % of defect areas, respectively (Figure 1). These results indicated that wet cleaning effectively reduced the defects; however, no obvious correlation was observed with the HSP values. Toluene

combined with SC-1 solution reduced the defects area to 0.3 % (Figure 1). This result can be attributed to cleaning and the addition of a silanol functional group on the SiO_2 surface by a SC-1 solution, as reported by Hinckley et al. [1].

The combination of a solvent and an inorganic cleaning solution effectively repaired defects in ODTS SAMs, and a defect-free monolayer will be obtained by optimizing the cleaning solution.

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ALE-SuP-17 Atomic Layer Etching of ITO, *Christoffer Kauppinen,* VTT Technical Research Centre of Finland

Indium tin oxide (ITO) is a degenerate n-type semiconductor often used as a transparent conductor. Oxide semiconductors like ITO are being studied for monolithic 3D integration on CMOS transistors, but to make ITO transistors with high on/off ratio the ITO channel needs to be thinned. This poster presents our recently published work of ITO ALE using thermal surface modification with BCl_3 and modified surface removal using Ar plasma. High synergy of 82% is obtained at 150℃. The etch per cycle (EPC) is 1.1 Å. The surface modification step exhibits excellent self-saturation and the modified surface removal step has a suitable self-saturation window. The ALE was developed in a conventional reactive ion etching (RIE) system. The developed ITO ALE was used to pattern ITO with conventional photoresist as the etch mask, and the etched areas are smoother than unetched areas, which is charasteristic of an ideal ALE process. The low-processing temperature, conventional photoresist compatible as etch mask, smoothening of the etched surfaces, and the use of conventional a RIE system make the ITO ALE process suitable for ITO transistor trials and fabrication.

ALE-SuP-18 Isotropic Atomic Layer Etching of Titanium Carbide Using Plasma-Exposure and Infrared Heating, *Kazunori Shinoda,* Hitachi High-Tech Corp., Japan*; T. Nguyen,* Nagoya University, Japan*; Y. Kozuma, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic atomic layer etching (ALE) is crucial for the advancement of the semiconductor industry, particularly due to the integration of three-dimensional high aspect-ratio structures in next generation devices. A notable method for achieving isotropic ALE is the plasma-assisted thermal cyclic ALE, which uses plasma exposure for the modification step and infrared heating for the desorption step. This method allows precise control over etching characteristics, such as material selectivity and surface roughness, by independently adjusting the temperatures for the modification and desorption steps. This control offers a high degree of tunability in etching parameters. A specialized 300-mm tool, namely dry chemical removal (DCR) apparatus, which comprises an inductively coupled plasma source and infrared lamps, has been developed to support this process. Over recent years, selective ALE of various materials, including Si_3N_4, SiO_2, TiN, W, and Co, has been demonstrated using the DCR apparatus. This paper presents the plasma-assisted thermal cyclic ALE of titanium carbide (TiC), commonly used in metal gate materials. To explore the etching mechanism, the experimental setup included a reaction chamber and *in-situ* X-ray photoelectron spectroscopy. Several TiC samples were exposed to radicals generated from the plasmas of fluorocarbon-based gas mixtures at a stage temperature of −20 °C. After plasma exposure, Ti 2p peaks indicating Ti–F bonds were observed, suggesting the formation of a titanium fluoride-based modified layer on the TiC surface. This modified layer desorbed from the TiC surface upon heating the samples at 100 °C, as evidenced by the disappearance of the Ti-F bond peaks. Cyclic etching tests were conducted by alternating between plasma exposure and infrared heating using the 300-mm DCR apparatus. The etching depth of TiC increased with the number of cycles, with an etched amount of 1.3 nm per cycle. The etching depth per cycle exhibited saturation behavior relative to the plasma-exposure time. Additionally, tests on stage temperature dependence revealed that self-limiting behavior was achieved only at a stage temperature as low as −20 °C, indicating that maintaining a low stage temperature is critical to prevent the desorption of reaction products during the surface modification step.

ALE-SuP-19 Atomic Layer Etching of Tantalum Nitride with Surface Fluorination Using Nf₃ or Cf₄ Plasmas, *H. Kang,* **Minsung Jeon,** *H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

A comparative study on atomic layer etching (ALE) process window was carried out for tantalum nitride (TaN) using nitrogen trifluoride (NF_3) and carbon tetrafluoride (CF_4) plasmas. The TaN surface was fluorinated with NF_3 or CF_4 plasmas and the fluorinated surface was subsequently removed by Ar ion sputtering. The chemical composition and bonding of the fluorinated layer were confirmed using x-ray photoelectron spectroscopy (XPS). The Ta-F_x bonds were identified in NF_3 plasma fluorination layer and Ta-F_x/Ta-C_x bonds were identified in CF_4 plasma fluorination layer. The depth of fluorinated layer was examined at various plasma exposure times using secondary ion mass spectrometry (SIMS). The fluorination depth reached a conversion depth of 8.4 nm for NF_3 plasma and 7.8 nm for CF_4 plasma. The depth of the fluorinated layer by NF_3 plasma was slightly deeper than that by CF_4 plasma at the same fluorination time.This result can be attributed to the Ta-C_x bonds on the surface, which inhibit the diffusion of fluorine (F) radicals. In the removal step, a wider ALE process window was observed at 50 – 90 V with NF_3 plasma compared to CF_4 plasma at 70 – 90 V. The difference in ALE ion energy window can be attributed to the difference in electronegative energy between Ta-F layer formed by NF_3 plasma and Ta-F_x/Ta-C_x layer formed by CF_4 plasma. The etch per cycle (EPC) of TaN was saturated at 180 sec of Ar ion sputtering for both NF_3 and CF_4 plasma. After the ALE process, the F residue remained at 5% on the TaN surface fluorinated with NF_3 plasma, whereas it was 3% in CF_4 plasma.

Plenary Session
Room Hall 5A - Session PS-MoM

Plenary Session

Moderators: Markku Leskelä, University of Helsinki, Finland, **Mikko Ritala**, University of Helsinki, **Fred Roozeboom**, University of Twente and Carbyon B.V., The Netherlands, **Dmitry Suyatin**, AlixLabs A.B.

8:45am **PS-MoM-1 ALD Welcome and Introductory Remarks**, *Mikko Ritala, M. Leskelä,* University of Helsinki, Finland

9:00am **PS-MoM-2 Opening Remarks: 50 Years of ALD**, *Tuomo Suntola, .,* Finland   **INVITED**

9:15am **PS-MoM-3 ALD: A Disruptive Technology Enabling New Device Architectures**, *Ivo Raaijmakers,* ASM, Netherlands   **INVITED**
For 3 decades ALD has been a crucial technology for scaling in the semiconductor industry. Many new device architectures, such as FinFET, Gate-All-Around, VNAND, and High Aspect Ratio DRAM can only be made by using the differentiated capabilities of ALD and PEALD, being conformality, uniformity, composition control, and relatively low process temperatures. Through academic and industrial R&D the materials capability and productivity of ALD and PEALD has been further improved which has caused the number of ALD layers in a chip to increase exponentially. This market pull - technology push tandem has propelled the ALD and PEALD market to grow to be among the largest deposition segments. In this presentation these developments will be reviewed, and a vision will be offered what is to come in the next decade for this pivotal technology for the semiconductor industry.

10:00am **PS-MoM-6 ALD 2024 Innovator Awardee Talk***: To Grow and* **Not To Grow: Exploring Mechanisms during Atomic Layer Deposition**, *Annelies Delabie,* imec and KU Leuven (University of Leuven), Belgium   **INVITED**
Electronic devices have become indispensable in our society as they affect important sectors such as communication, healthcare, education, transport, and energy. The expanding computing power and memory result from a spectacular evolution from planar micro-electronic devices to 3D nano-electronic devices. Today, the industry is moving to a transistor design that consists of stacked nanosheet channels and we are researching an even more complex geometry where the negative and positive channels are stacked on top of each other; the so-called complementary field effect transistor (CFET). To achieve the latter, we need to create semiconductor, dielectric, and metal patterns with nanoscale thickness and precision on horizontal and vertical sides of 3D structures.

Atomic layer deposition (ALD) is and will remain an enabling technique in electronic device fabrication. The cyclic process based on self-limiting surface reactions of gas phase precursors provides inherent growth control below the nanoscale and excellent conformality. A valuable emerging capability is to grow material only where needed, on a given area of a patterned substrate by area-selective ALD, which has great potential to improve or simplify the device fabrication. One key aspect for realizing (sub-)nanometer-thin continuous layers as well as area-selective deposition is the reactivity of the initial surface. The predominant process during ALD is fast precursor adsorption. Still, the initial substrate surface may react differently than the ALD grown material. When it is less reactive, it may not be covered after the first ALD cycle, and several cycles may be needed to close the layer. During this initial nucleation and growth regime, the changing surface composition affects the deposition by a complex interplay of processes, providing challenges and opportunities to modulate growth.

Rational process design based on mechanistic understanding can enable modulations from continuous nanometer-thin layers to sparse nanoparticles to area-selective deposition. This presentation therefore discusses mechanisms during the initial stages of ALD and area-selective ALD of dielectrics, conductors, and 2D materials. Experiments combined with modeling reveal various growth evolutions for different processes and substrates. On surface areas with low surface energy, adsorption may compete with surface diffusion and aggregation of adspecies. Diffusion can be leveraged to enhance selectivity on patterns with nanoscale dimensions. For 2D materials, understanding enables tuning the crystal size, location, and ultimately crystal shape and orientation, an exciting outlook for emerging devices and other applications.

11:00am **PS-MoM-10 ALE Welcome and Introductory Remarks**, *Fred Roozeboom,* University of Twente and Carbyon B.V., The Netherlands; *D. Suyatin,* AlixLabs A.B., Sweden

11:15am **PS-MoM-11 Atomic Layer Precision Process to Enable Advanced Patterning toward High-NA EUV Era**, *Eric Liu,* Tokyo Electron America
                                                                              INVITED
As the semiconductor industry aims to achieve higher resolutions in device patterning, the need for advanced lithography techniques becomes more imperative. Extreme ultraviolet (EUV) lithography is a promising solution with high-resolution capabilities to resolve the projection pattern on the wafer. Next-generation high-NA (numerical aperture) EUV lithography further enhances the imaging resolution to a smaller feature size. Still, the conventional plasma etching methods have presented challenges regarding pattern transfer from the lithography. Atomic layer precision etches, such as atomic layer etch (ALE), is a needed technology for EUV pattern transfer, as it can deliver high precision by controlling the pattern variations and etching selectivity with minimal damage to the masking/underlying material.

In this study, we investigate the effectiveness of these etching techniques for both EUV single exposure and double patterning applications. In EUV single exposure, atomic precision etching provides a high degree of control over critical dimension uniformity and pattern transfer fidelity. Using a combination of the ALE concept and advanced plasma species control, we demonstrate the ability to achieve high selectivity among challenging materials such as the photoresist and underlaying material and improve the pattern variation.

In EUV double patterning, our challenges are quite different from the EUV single exposure. The two unique challenges are [1] aggressive critical dimension shrink from lithography to etch and [2] narrow spacing issues. The atomic precision etching techniques offer a pathway to pitch splitting and pattern multiplication while maintaining high resolution and low line edge roughness. We present a novel approach based on alternative selective and anisotropic etching cycles to achieve pitch division with atomic precision when the space of the feature is under 10 nm. Overall, our results demonstrate the significant potential of atomic layer precision etch in enabling the development of advanced lithography techniques for next-generation semiconductor devices.

ALD Applications
Room Hall 3D - Session AA1-MoA

Energy: Batteries and Energy Storage
Moderators: Christian Dussarat, Air Liquide Laboratories, **Jin-Seong Park**, Hanyang University

1:30pm AA1-MoA-1 Enabling Fast Charging of Lithium-ion Batteries at Sub-Zero Temperatures with ALD coatings, *T. Cho, Y. Chen, D. Liao,* University of Michigan; *E. Kazyak,* University of Wisconsin; *D. Penley,* **Neil P. Dasgupta,** University of Michigan

Increasing the achievable charging rate of lithium-ion batteries (LIBs) is critical to the widespread commercialization of electric vehicles (EVs). However, it becomes increasingly challenge to charge batteries at low temperatures (< 5 °C), which is a major challenge facing adoption of EVs in cold climate

The primary factor limiting the ability of state-of-the-art LIBs to charge under both high-rate and low-temperature conditions is the propensity for Li metal to plate out on the graphite surface during charging.[1] The poor reversibility of Li metal in LIB electrolytes leads to rapid capacity fade, consumption of the electrolyte, and safety concerns. This problem is exacerbated in high-energy density cells with thicker electrodes, leading to energy-power tradeoffs.

To mitigate these effects, we have previously demonstrated that Li plating can be significantly suppressed during fast charging by implementing an atomic layer deposition (ALD) surface coating of a lithium borate-carbonate (LBCO) solid electrolyte directly onto calendered graphite anodes[2]. This ALD single-ion conductor has previously been shown to exhibit ionic conductivities above 2×10^{-6} S/cm and excellent electrochemical stability, including with Li metal.[3] In comparison to uncoated control electrodes, the LBCO a-SEI coating: 1) eliminates natural SEI formation during formation cycles, 2) decreases interphase resistance by >75% compared to that of the natural SEI, and 3) extends cycle life significantly under fast-charging conditions.

Building upon this demonstration of improved fast-charge ability with ALD coatings, in the current study, we demonstrate the ability of an artificial SEI layer deposited by ALD to also enable fast charging at sub-zero temperatures (down to -10 °C) while maintaining extreme fast charging rates (up to 6C) without Li plating[4]. This remarkable result is enabled by a synergistic combination of interfacial modification by ALD and fabrication of 3-D architected electrodes. These results demonstrate the power of decoupling interfacial and bulk mass transport effects under extreme charging temperatures, providing new fundamental insights into the factors that limit performance and result in cell degradation. In the future, the ability to fast-charge LIBs in cold environments will accelerate electrification of technologies in a broader range of geographic locations.

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3. E. Kazyak et al., *J. Mater. Chem. A* **6**, 19425 (2018)
4. T. H. Cho, Y. Chen, D. W. Liao, E. Kazyak, D. Penley, N. P. Dasgupta, *Submitted* (2024)

1:45pm AA1-MoA-2 Atomic Layer Deposition of Lithium Borate and Borophosphate Thin Films for Lithium-ion Battery Applications, *Tippi Verhelle, A. Dhara, L. Henderick,* Ghent University, Belgium; *J. Meersschaut,* IMEC Belgium; *J. Dendooven, C. Detavernier,* Ghent University, Belgium

Lithium-ion batteries (LiBs) play a vital role in modern society, but challenges arise from unwanted side-reactions at the electrolyte/electrode interface. A promising solution to this issue involves the application of an ultrathin, protective coating on the electrode using atomic layer deposition (ALD). Previous studies highlight ALD's effectiveness in addressing such challenges, emphasizing thickness control and conformality [1]. Our research focuses on advancing this strategy by developing lithium borophosphate as a coating material for enhanced LiB performance.

In the work of Kazyak et al. [2], who used ALD to obtain a lithium borate-lithium carbonate intermixed material, the potential use of lithium borates (albeit with carbon inclusion) was evidenced. In this work, we aimed to achieve ALD of pure lithium borate films, which served as a starting point for new and optimized lithium borate mixtures towards even more controlled electrochemical properties. Our aim is to intermix this pure lithium borate with lithium phosphate, leveraging the latter's stability. Despite lithium phosphate's inherently lower ionic conductivity, namely 1.4

$\times 10^{-10}$ S cm^{-1} as deposited by ALD [3], studies using other deposition techniques have demonstrated that combining it with lithium borate effectively enhances the conductivity [4].

Our research introduced a new process for depositing lithium borate, utilizing lithium bis(trimethylsilyl)amide (LiHMDS), H_2O and trimethylborate (TMB). At 250°C, the process exhibited linear growth, with a growth per cycle of 0.04 nm, and saturation for every precursor step (Fig. 1). This process displayed a variation in composition as indicated by ERD (Fig. 2) and electrochemical properties at different deposition temperatures. With impedance spectroscopy (EIS), we calculated the conductivity of an 80 nm lithium borate thin film deposited at 250°C to be $1.60 \pm 0.03 \times 10^{-7}$ S cm^{-1} at 30°C, with an activation energy of 0.58 ± 0.01 eV (Fig. 3).

Integrating this lithium borate with the well-known lithium phosphate process [5] was achieved through a supercycle approach. Varying the number of lithium phosphate subcycles relative to a constant number of lithium borate subcycles resulted in coatings with distinct electrochemical behavior. Our findings offer practical insights for tailoring LiB coatings with controlled electrochemical properties, contributing to advancements in battery technology.

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2:00pm AA1-MoA-3 Fluorine-free ALD Process Produces Fluorine-rich Cathode Electrolyte Interphase for Lithium Batteries, *Giulio D'Acunto, S. Shuchi,* Department of Chemical Engineering, Stanford University; *Y. Cui,* Department of Materials Science and Engineering, Stanford University; Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; Department of Energy Science and Engineering, Stanford University; *S. Bent,* Department of Chemical Engineering, Stanford University; Department of Energy Science and Engineering, Stanford University

The continuous evolution of lithium-ion and lithium-metal batteries is pivotal for meeting the growing demands of high-performance energy storage systems. Central to this advancement is the enhancement of the cathode-electrolyte interphase (CEI), a critical component in determining battery efficiency and safety. A fluorine-rich CEI is widely recognized for its role in enhancing Li$^+$ ionic conductivity and chemical stability. A fluorine-rich CEI is typically achieved by using fluorinated solvents, fluorinated additives, or an artificial SEI comprised of fluorinated materials. This research introduces an innovative approach to CEI improvement through the application of atomic layer deposition (ALD). Our design approach aims to utilize i) the high reactivity of the ALD precursors toward the existing cathode binder (polyvinylidene fluoride, PVDF), and ii) the surface acidity of the deposited thin film to induce more anion decomposition, further enhancing the fluorination of the CEI.

Leveraging the nanoscale precision and uniformity of ALD, we chose to develop a LiAl$_x$O$_y$ coating on lithium-nickel-manganese-cobalt-oxide (NMC) cathodes. Li(HMDS) and TMA are used as metal precursors and water as a co-reactant. An M1-O-M2-O super-cycle, where M1 and M2 refer to the metal precursors, and O represents water, is used for the LiAl$_x$O$_y$. After exploring process parameters to enhance Li content and achieve saturation, the coated NMC cathode was characterized by angle-resolved X-ray photoelectron spectroscopy (ARXPS). We found evidence of Li-F species comprising nearly 50% of the total fluorine species, in contrast to less than 10% for the uncoated NMC cathode. The effectiveness of the fluorine-rich coating was then evaluated with electrochemical measurements, comparing the ALD-coated NMC to the bare NMC. The capacity retention of the coated cathode outperforms by almost a factor six that of the bare cathode, using a baseline carbonate-based electrolyte. Moreover, the characterization of the CEI after 50 cycles in the battery shows that i) the F-rich ALD coating is preserved during cycling, working as an artificial CEI, and ii) the native CEI overlayer atop the ALD layer is more fluorinated due to the surface acidity impact. This novel approach using ALD to achieve a fluorine-rich artificial CEI via a fluorine-free cathode coating process offers a more environmentally friendly approach compared to traditional methods.

2:15pm AA1-MoA-4 Atomic Layer Deposition of Interface-Engineered $Li_4Ti_5O_{12}$: Toward High-Capacity 3D Thin-Film Batteries, *Jan Speulmanns*, S. Bönhardt, M. Czernohorsky, W. Weinreich, Fraunhofer Institute for Photonic Microsystems IPMS, Germany

Atomic layer deposition (ALD) of Li-compound thin films has aroused significant interest in recent years. Promising applications are Li-ion thin-film batteries (TFBs), protective particle coatings, and neuromorphic computing. Here, we evaluate $Li_4Ti_5O_{12}$ (LTO) fabricated by ALD for 3D solid-state TFBs to power upcoming autonomous sensor systems.

The simultaneous increase of power and energy density of 3D TFBs can be achieved by coating the battery layer stack over microstructured substrates. The required conformal, pinhole-free deposition and stoichiometric control of nanometer-thin films on highly structured surfaces are only accessible via ALD. However, direct ALD of Li-compound anodes remains challenging.

In previous studies, we developed a thermal three-step ALD process for Li-containing oxides on 200 mm Si wafers. Lithium-tert-butoxide (LTB) and lithium hexamethyldisilazide (LiHMDS) were proven as suitable precursors, forming spinel LTO with low impurities. The excellent electrochemical behavior of LTO with LiHMDS was linked to the film texture.

In this work, we optimize the LTO ALD process with LTB toward 3D TFBs and evaluate the electrochemical performance for the first time. A process with a saturated growth per cycle of 1.06 Å $cycle^{-1}$ for 7 s LTB pulses was developed. An ALD temperature window between 240 and 320 °C was identified. The effect of the substrate on the initial growth and crystallization behavior was investigated. The crystallization-inhibiting effect of the titanium nitride current collector is suppressed by introducing an AlO_x interlayer.

Planar LTO films with various thicknesses of up to 75 nm were manufactured by ALD, increasing the footprint capacity from 1.5 to 4.3 µAh cm^{-2}. However, the C-rate performance of thicker films is inferior due to the low conductivities of LTO. 50 nm films demonstrate the optimum energy and power density. A footprint capacity of 1.95 µAh cm^{-2}, corresponding to 65 % of the theoretical capacity, was achieved at 50 C.

Next, we evaluate ALD LTO films as 3D TFB anodes. The conformality of the ALD process was improved by extending the LTB pulse and purge times to 11 and 20 s. The purge time is the key factor enabling a step coverage of 70 % for holes with an aspect ratio of 10:1. 3D samples with an area-enhancement factor of 9 obtained a footprint capacity of 19.8 µAh cm^{-2} at 1 C. The large capacity increase by a factor of 6.75 compared to planar samples is according to the conformality. The power performance of 3D LTO samples at high C-rates will be discussed. The superior performance of ALD LTO is a key enabler for high-volume production of on-chip high-capacity 3D TFBs.

2:30pm AA1-MoA-5 ALD for Advanced Lithionic Devices: Hybrid Ultrathin Solid-State Electrolytes, *Ilyass GHANDARI*, N. GAUTHIER, S. POULET, CEA-LETI, France; *M. BECHELANY*, CNRS, France; *M. BEDJAOUI*, CEA-LETI, France
Innovative micro-supercapacitors (MSCs) such as LiPON based MSCs are emerging to address the technological challenges faced at higher frequencies (>kHz),especially energy harvesting and storage, which requires efficient materials coupled with improved microfabrication techniques to unlock the full potential of such devices. In this way, conformal and self-limiting surface reactions enabled by Atomic Layer Deposition (ALD) give great advantages to form and optimize Lithium based thin films compatible with complex geometries. Here in, a multidisciplinary approach was conducted to develop the thermal ALD process, characterize the physico-chemical properties and evaluate the electrical performances of nano-hybrid Solid State Electrolytes (SSE).

The thermal ALD process for ultrathin LiPON films (<25nm) is realized using Li-Bistrimethylsilylamide (LiHMDS) and Diethylphosphoramidate (DEPA) precursors in a deposition temperature range 300-350ºC. To further optimize LiPON's electrochemical performances, Trimethyl Aluminium (TMA) and H_2O were pulsed to incorporate Al_2O_3 in SSE films. Ellipsometry was used to calibrate the growth rate of LiPON-based films. The microstructure was analyzed by X-Ray Diffraction (XRD) to highlight the amorphous nature of the thin films, indicating that the Al_2O_3 incorporation preserves favorable amorphous structure, which is a key characteristic for achieving excellent electrochemical performances [1]. The XPS spectra show typical core peaks (Li_{1s}, P_{2p}, O_{1s}, N_{1s}, Al_{2p}) corresponding to different LiPON based samples. The analysis reveals that Al_2O_3 insertion seems to impact the nitrogen environment. From N1s spectra (Fig.1), the peaks present two main components located at 397 eV and 399 eV, attributed respectively to a divalent nitrogen state (N_d) and a trivalent nitrogen state

(N_t) [1], whose proportion evolves as a function of Al_2O_3 incorporation. Thus, the concentration of divalent nitrogen becomes predominant over trivalent nitrogen, inducing an increase in the N_d/N_t fraction when more Al_2O_3 is introduced. This variation has frequently been reported as a major factor in improving Li-ion mobility [1]. The Electrochemical Impedance Spectroscopy (Fig.2) addresses the changes in Li-ion conductivity of the LiPON films upon addition of Al_2O_3 concentration.

This work provides a solid ALD approach with promising potential to optimize the electrical performances (ie Li^+mobility, areal capacitance etc) in ultrathin SSE, shedding light on the application of such hybrid microstructures in several Lithionic devices such as micro-supercapacitors, micro-batteries and transistors.

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2:45pm AA1-MoA-6 Low Temperature ALD of Vanadium Sulfide (Ultra)thin Films for Nanotubular Supercapacitors, *Raul Zazpe*, M. Sepulveda, J. Rodriguez-Pereira, L. Hromadko, M. Kurka, H. Sopha, J. Macak, University of Pardubice, Czechia
Metal sulfides (MSs) are materials exhibiting a great variety of interesting inherent properties including semiconducting nature, high electrical conductivity and capacitance, (photo)catalytic capability, excellent redox reversibility and their abundance and low-cost.[1] Thus, MSs nanomaterials are a prospective alternative in multidisciplinary applications demonstrating a promising performance in energy conversion and energy storage devices[1] sensors,[2] photodetectors,[3] and biomedical applications[4] among others. Among the wide range of MSs, vanadium-based materials exhibit outstanding electrical conductivity and capacitance together with an excellent redox reversibility and electrochemical properties.[5] Vanadium is an abundant element that exhibits multiple oxidation states, which provides a rich and versatile chemical reactivity. Consequently, vanadium sulfides have been explored as promising materials as electrode material for supercapacitors (SCs).[6]

Herein, we present for the first time the synthesis of vanadium sulfide (V_xS_y) by Atomic Layer Deposition (ALD) based on the use of tetrakis(dimethylamino) vanadium (IV) and hydrogen sulfide.[7] The (ultra)thin films V_xS_y are synthesized in a wide range of temperatures (100 - 225 °C) and extensively characterized by different methods. The chemical composition of the V_xS_y (ultra)thin films reveals different vanadium oxidation states and sulfur-based species. Extensive X-ray photoelectron spectroscopy analysis studies the effect of different ALD parameters on the V_xS_y chemical composition. We further explore the electrochemical properties of ALD V_xS_y (ultra)thin films as electrode material for supercapacitors by coating TiO_2 nanotube layers (TNTs) with different numbers of V_xS_y ALD cycles at 100 °C. Long-term cycling tests reveal a gradual decline of electrochemical performance due to the progressive V_xS_y thin films dissolution under the experimental conditions. Nevertheless, V_xS_y coated TNTs exhibit significantly superior capacitance properties, as compared to the blank counterparts. The enhanced capacitance properties exhibited are derived from the presence of chemically stable and electrochemically active S-based species on the TNTs surface.

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3:00pm AA1-MoA-7 Boosted Zn^{2+} Storage Performance of Hydrated V_2O_5 by Defect and Heterostructure, *V. Nguyen, J. Kim, Seung-Mo Lee,* Korea Institute of Machinery & Materials (KIMM), Republic of Korea
The inherent sluggish Zn^{2+}diffusion and poor electronic conductivity limit the ion intercalation/deintercalation process in aqueous Zn-ion batteries (ZIBs) using an oxide-based cathode. Here, we demonstrated that a heterostructure in the form of defective hydrated V_2O_5 embedded in the porous carbon textile (d-VOH@CT) could tackle these issues. To obtain the d-VOH@CT heterostructure, a V_2O_5 layer was deposited on waste cotton textiles using atomic layer deposition (ALD), followed by pyrolysis. The carbothermic reduction of V_2O_5 ($C + V_2O_5 \rightarrow C' + V_2O_3 + VC + CO/CO_2(g)$) coated on cotton textile transformed the cotton into the porous carbon textile covered with a hybrid VC/V_2O_3 layer. In the air, this VC/V_2O_3 layer was naturally oxidized to defective hydrated vanadium oxide (d-VOH) flakes embedded in the porous carbon textile (CT). The additional edges created

by crystal defects significantly promoted facile Zn-ion adsorption and intercalation. Expanded interlayer spacing and reduced crystalline domain size kinetically facilitated fast Zn-ion diffusion in d-VOH flakes with shortened diffusion paths. Moreover, the heterostructure of d-VOH on the conductive carbon textile triggered rapid charge transfer, leading to high rate capability and structural stability. The ZIBs fabricated using the d-VOH@CT cathode delivered a preferable reversible capacity of 416 mA h g^{-1} at 0.1 A g^{-1}, an impressive energy density of 293 W h kg^{-1}, and a long cycle life. In addition, the d-VOH@CT heterostructure was able to be used as a freestanding cathode for a flexible ZIB with outstanding mechanical robustness and electrochemical stability.

3:15pm **AA1-MoA-8 High Throughput Atomic Layer Deposition of Niobium Oxide Thin Film for Lithium-ion Battery Application**, *S. Kamimura, C. Dussarrat,* Air Liquide Laboratories, Japan*; **Nicolas Blasco,** Air Liquide Advanced Materials, France*

Surface modification of cathode active materials (CAMs) by atomic layer deposition (ALD) is known to improve the structural stability, ionic interfacial conductivity, and consequent charge-discharge characteristics of lithium-ion batteries (LiBs). The powder ALD technique has been shown to be highly effective in producing inorganic films, even on the particles of CAMs, with high conformality, uniformity and self-limiting growth, providing exceptional control over film thickness down to sub-nanometer level. Although the current powder ALD technique can successfully handle large amounts of nanoparticles for conformal coating with ALD, it requires a large amount of precursor for high surface area when working with fine particles, causing unique challenges for the ALD precursor. The dosage of the precursor/co-reactant is directly related to the surface area of the particles; the larger the area, the longer the exposure time required, resulting in a longer process time. Therefore, an ALD precursor that enables a high growth rate of inorganic thin films is in high demand.

We have conducted the synthesis screening of several types of organometallic niobium precursors for ALD and have successfully deposited an ALD Nb_2O_5 film using an organometallic precursor called Nautilus. This precursor showed a higher volatility & higher growth rate than tris(diethylamide)(tert-butylimido)niobium (TBTDEN). The Nb_2O_5 thin film growth on Si wafer was evaluated by QCM, XPS and ellipsometry measurements, and an outstanding GPC of 2 Å/cycle was determined at 225 $^{\circ}$C, increasing with reactor temperature while maintaining excellent step coverage.

Powder ALD with Nautilus precursor was performed at 250 $^{\circ}$Cusing a fluidized bed reactor to achieve uniform Nb_2O_5thin film coating on CAMs. The TEM/EDS analysis shows that the entire surface of CAMs particles was uniformly covered with Nb_2O_5thin film with a thickness of ~1 nm even after 3 ALD cycles. The electrochemical performance measurements were conducted in R2032 coin-type cells (half cell). We clearly found that the Nb_2O_5thin film coating can suppress undesirable side reactions such as electrolyte decomposition on CAMs, and lead to the long-term cycle stability of discharge capacity. In the presentation, we will introduce the ALD characteristics of Nautilus and its LiB performance evaluation.

ALD Applications
Room Hall 3D - Session AA2-MoA

Applications in ULSI FEOL: Gate Electrodes & Contact Metals, High-K, and 3D Transistor Fabrication

Moderators: Scott Clendenning, Intel Corporation, **Christian Wenger**, IHP - Leibniz Institut fuer innovative Mikroelektronik

4:00pm **AA2-MoA-11 Thermal Atomic Layer Deposition of Boron Containing Oxide Films as Solid Sources for Doping of Advanced Memory Devices**, *Y. Shen,* Beijing Superstring Academy of Memory Technology, China*; S. Yang,* Institute of Microelectronics, China*; **Jinjuan Xiang,** Beijing Superstring Academy of Memory Technology, China*; J. Liu, J. Gao,* Institute of Microelectronics, China*; G. Wang, C. Zhao,* Beijing Superstring Academy of Memory Technology, China

In recent decades,with the continuous scaling downof devicedimensionsand the emergence of complex three-dimensional structures,conventional ion implantation cannot meet the requirements of non-damage and uniform doping of the nonplanar transistor architecture. Atomic layer deposition (ALD) is one of the mostpromising methods for forming controlled and conformal dopant-containing layer. Compared to plasma enhanced ALD, thermal ALD has better ability for achieving the required conformity conditions and high scalability for 3D structures with

higher AR ratio. By combing of ALD with the heat-driven annealing,non-damage and conformal doping in Si can be achieved. However, ALD doping still faces many challenges, one of the big issues is that B_2O_3 films cannot grow sustainably, which hinders its further application [1, 2].

In this paper, Al_2O_3 and SiO_2 layer were used as enhance layer to promote the deposition of B_2O_3 by thermal ALD. By using Al_2O_3 interlayer, low lewis acidity of Al−OH- was formed. Boron is evenly distributed in $B_xAl_{1-x}O_y$ film with a content of about 15 at. %, which is higher than that in $B_xSi_{1-x}O_y$ film. After rapid thermal annealing, the maximum doping concentration of B can reach 2E20 atom /cm^3, and the doping concentration of Al in Si is low. When SiO_2 as the enhance layer, the maximum B doping concentration is 3E19 atoms /cm^3. In addition, the content of B in $B_xSi_{1-x}O_y$ film and doping concentration in Si are higher at low B:Si ratio of 4:3 than at B:Si of 5:1, which is mainly due to the fact that enough SiO_2 layer can promote the growth of B_2O_3 more effectively. Uniform and dose-controlled doping achieved by this thermal ALD doping is believed to have great application prospects in 3D structures device, especially for vertical stacked dynamic random-access memory (DRAM).

4:15pm **AA2-MoA-12 Plasma-Enhanced ALD of Thin Conductive Cu Films**, *Maria Gabriela Sales, N. Nepal, P. Litwin, D. Boris, S. Walton, V. Wheeler,* U.S. Naval Research Laboratory

Interconnect vias are conduits that transport signals between circuit components, and are typically made of Cu due to its low resistivity, high thermal conductivity, low coefficient of thermal expansion, high melting temperature, and good mechanical properties. Traditionally, Cu interconnect vias are fabricated through electrochemical deposition which is followed by chemical mechanical polishing and various cleaning steps to get the Cu mostly conformal with the via structure. However, these processes tend to leave behind voids in the via and/or leftover Cu in areas with unwanted Cu growth. Atomic layer deposition (ALD) is a promising alternative technique to avoid such reliability issues because it is a saturating and self-limiting deposition process. Furthermore, the layer-by-layer nature of ALD allows for precise thickness control, which is an important consideration in the scaling of circuit components.

For proper implementation of ALD in the deposition of via structures, we need to study the key ALD processing conditions that produce Cu thin films with the desired chemical and physical properties and optimal electrical performance. In this work, we study a plasma-enhanced Cu ALD process in a Veeco Fiji G2 reactor equipped with a turbo pump and substrate biasing, using copper(I)-N,N'-di-sec-butylacetamidinate, or [Cu(^{s}Bu-amd)]$_2$, as our Cu precursor and H_2 plasma as our reducing reactant. We present a parametric study where we investigate the different growth conditions, i.e., growth temperature, precursor pulse, composition of gases in the plasma, and plasma power, among others, and observe how they affect Cu film growth. In-situ ellipsometry is used to monitor growth rate, post-deposition X-ray photoelectron spectroscopy (XPS) is used to analyze the film and interface chemistry, and atomic force microscopy (AFM) is used to examine the resulting film morphology. Initial results show metallic Cu films were successfully deposited using a 300 W Ar/H_2 plasma with a 20% Ar flow fraction and a 10-second plasma pulse duration. This demonstrates the feasibility of this PEALD Cu process; however, to-date films are limited in thickness, and possible approaches to overcome these issues will be discussed.

4:30pm **AA2-MoA-13 Selective Atomic Layer Deposition of Ultra-Thin Ru on W for Metal Contact**, *Rong Chen, Z. Qi, E. Gu,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; B. Shan,* State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China*; K. Cao,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

Atomic selective area layer deposition (ASD) of ruthenium has attracted considerable interest for various applications in nanoelectronics and due to its potential role in front-end-of-line (FEOL) contact in future technology nodes. In this talk, it provides insight into the effects of discrete feeding atomic layer deposition (DF-ALD) process and post-processing treatments on the nucleation of Ru film and selective growth on W/SiO2. DF-ALD process can improve the purging of excess physically adsorbed precursors, provide more reaction sites, and increase the nucleation density. With DF-ALD, ultra-thin and low-resistivity Ru thin film on W contact was obtained. According to KMC theoretical calculations, when there are excess physical

adsorption precursors and chemically adsorbed reaction by-products around the reaction site, there is a lack of steric hindrance required for chemical reactions and the reaction is difficult to occur. Due to the size-dependent mobility of nanoparticles and differences in substrate adsorption energy, post-processing more easily promotes nucleation defects in non-growth areas migration to the growth area. It is an effective way to eliminate non-growth area defects and amplify selectivity. The inherently selective ALD process is successfully transferred onto W/TiN/SiO$_2$ nanopatterns with ~100 nm pitch and obtained high selectivity with 5–6nm films on W and no defects in the SiO$_2$ and TiN regions. The results indicate that inherently selective ALD is a robust and general tool that has excellent application prospects in FEOL processes, which provides an innovative avenue for self-aligned nanostructures.

4:45pm AA2-MoA-14 Effect of High Precursor Dose on the IZO Film Property Uniformity Within Wafer Deposited by Thermal ALD, *Yuting Chen, P. Yuan, X. Ma, Z. Jiao, Y. Shen, L. Chai, J. Xiang, M. Zeng, H. Sun, G. Wang, C. Zhao,* Beijing Superstring Academy of Memory Technology, China

Recently, IGZO-based vertical channel-all-around (CAA) thin-film transistors (TFT) for 2T0C dynamic random access memory (DRAM) with better density advantages has attracted wide attention. Zinc-doped In$_2$O$_3$ (IZO)is a potential gate electrode material for CAA TFT device, because of its relatively low resistivity, and low process thermal budget, which is perfectly suitable for IGZO-based devices. IZO material property deposited by ALD on 12-inch wafer has been rarely studied. Usually, to achieve better step coverage on high aspect ratio (AR) vertical structure, higher precursor dose is necessary, compared with the saturation dose obtained on planar structure. Hence, in this work, thermal ALD IGZO/Al$_2$O$_3$/IZO film stack, which simulated the gate stack in CAA TFT device, were employed as the vehicle to investigate the IZO film property at high precursor dose. Moreover, the samples of precursor inlet and outlet regions were analyzed to reveal the film uniformity within 12-inch wafer. Unexpectedly, the IZO film of inlet region has the worse electrical properties. Materials characterization were conducted to elucidate the mechanism of heterogeneity. Although XPS results shows no difference in the In/Zn composition ratio between the inlet region and the outlet region, XRD results shows higher In$_2$O$_3$ crystallinity in inlet region than outlet region, which is also confirmed by AFM scans. Based on these results, it can be inferred that high-dose precursor at the inlet position may lead to insufficient ALD reaction process, resulting in many defects in the IZO film and degraded electrical properties. The non-uniformity of IZO film poses some challenges for subsequent process integration, such as the CMP process.

This work highlights the significant impact of different regions within 12-inch wafer on the properties of films at high dose. In spite step coverage can be improved by increasing the precursor dose, too much precursor will lead to degenerated film at inlet region.

5:00pm AA2-MoA-15 Development of ALD Gate Dielectrics for TMD Nanosheet FETs, *T. Lee, B. Chao, Y. Chung, Y. Su,* TSMC, Taiwan; *B. Liu, C. Su, C. Kei,* Taiwan Instrument Research Institute, Taiwan; *C. Cheng, Pinyen Lin, I. Radu,* TSMC, Taiwan

Superior electrostatics control of monolayer (1L) TMDs holds great potential in advancing the scaling of nanosheet (NS) transistors in advanced technology nodes [1]. One critical aspect is to achieve a conformal dielectric layer on TMD NS channel using atomic layer deposition (ALD) [2]. The main challenge in achieving high-quality gate dielectrics is forming a good nucleation layer on the dangling bond-free TMD interface. This study successfully used the ALD technique to form a uniform AlOx thin film on 1L-MoS2 without damaging the material. Furthermore, good performance of MoS2 NS nFET is also successfully demonstrated.

5:15pm AA2-MoA-16 ALD in Semiconductor Logic Manufacturing: Challenges Met and Opportunities Ahead, *David Towner,* Intel Corp.
INVITED

Atomic Layer Deposition has played a unique, enabling role in the evolution of semiconductor logic device manufacturing.ALD's ability to bring atomic level control to thin film deposition is particularly critical to applications at the heart of transistor performance, such as High-K gate dielectrics and workfunction materials.With the progression to 3-D transistor structures like FinFETs and RibbonFETs, ALD's ability to conformally deposit on complex topography is unparalleled.This talk will present one industry expert's take on ALD's success stories as well as the many challenges ahead, including less glamorous but important factors such as cost and manufacturability.Special effort will be taken to highlight opportunities for further innovation as we continue to advance Moore's Law.

ALD Fundamentals
Room Hall 3A - Session AF-MoA

Precursors and Chemistry: Precursor Design, New Precursors, Process Development I
Moderators: Charles Dezelah, ASM, **Charles H. Winter**, Wayne State University

4:00pm AF-MoA-11 ALD of Copper and Bismuth Using Pinacolborane as a Reducing Agent, *Anton Vihervaara, T. Hatanpää, K. Mizohata, M. Ritala,* University of Helsinki, Finland

High quality metal thin films are an essential material class in the development of new technologies. Copper is the foremost interconnect material in microelectronics and though there is incentive to replace it with other metals, copper will remain an important metal for interconnects for the immediate future. Bismuth on the contrary is less commonly used thin film material but possesses many intriguing characteristics. It has many potential applications suggested in the literature including semiconductor devices, superconductors, and anodes for batteries. These applications require high-quality thin films deposited uniformly over large areas and on 3D structures.

Atomic layer deposition (ALD) is the best method for the manufacturing of complex 3D structures. Several ALD processes for Cu metal already exist, but new ones are constantly sought out to overcome limitations of the existing ones. Bismuth on the other hand does not have such a range of existing ALD processes. As far as we are aware, only one process can be found in literature. [1]

In order to deposit very thin but also completely continuous films, it is important to keep the deposition temperature low. Typically, lower deposition temperatures lead to smaller grains and thus to smoother films. We study novel ALD precursors with a focus on reducing agents, since they are less explored than the metal precursors. To our knowledge pinacolborane has not been used in ALD experiments before, though it has been suggested as a potential reducing agent [2]. Now we investigated it in actual ALD experiments with metal alkoxides. The idea behind using the pinacolborane is that the favorable formation of the strong B-O bond would strip alkoxide ligands from metal precursors.

In our study, pinacolborane was combined with two metal alkoxides, Cu(dmap)$_2$ and Bi(OCMe$_2^i$Pr)$_3$, to deposit the respective metals. Depositions were done at low temperatures of 80-130 °C for Cu and 90 °C for Bi. ALD characteristics were confirmed for the Cu deposition. At 100 °C growth rate of 0.12 Å/cycle was observed. Continuous film deposited at 100 °C had a resistivity of 4.2 µΩcm. Bismuth films were highly oriented and consisted of platelets parallel to the substrate surface. Both films contained only small amounts of impurities.

[1] Precursors and Processes for the Atomic Layer Deposition of Bismuth Metal Thin Films, Daniel Beh, Wayne State University; Z. Devereaux, T. Knisley, Applied Materials; C. Winter, Wayne State University, presented at the 23rd International Conference on Atomic Layer Deposition, Bellevue, July, 2023.
[2] Winter, C. H., Knisley, T. J. US Pat. Appl. Publ. US 2015/0167158 A1.

4:15pm AF-MoA-12 Ligand Optimization of Volatile Cobalt-Alkoxide ALD Precursor, *Atsushi Sakurai, A. Yamashita, T. Yoshino, Y. Ooe, K. Takeda, M. Enzu, M. Hatase, A. Nishida,* ADEKA CORPORATION, Japan

Co thin films have been applied for interconnect applications on many electronic devices to support Cu-based interconnects or to replace Cu itself with device miniaturization. It is extrapolated that the conventional CVD precursor, CCTBA: Co$_2$(CO)$_6$(^{t}BuC≡CH), could continue to assist in interconnect fabrication. Due to the poor reported thermal stability and area selectivity of CCTBA, however, there has been a great deal of effort to identify an improved Co precursor [1]. For example, Co-diazabutadiene is an attractive precursor to realize area selective Co film growth with thermal ALD processing [2]. CoCl$_2$(tmeda) [3], Co-amidinato [4], Co-cyclopentadienide [5] and Co-diketonato [6] were also investigated for specific process requirements. Despite significant development work on Cu-alkoxide precursors, Co-alkoxide precursors remain less documented in the literature [7].

This presentation will share the basic chemistry of Co-alkoxides and how to obtain high vapor pressure, which is a critical property for ALD film growth.

Monday Afternoon, August 5, 2024

In comparison with Cu-alkoxides, high vapor pressure Co-alkoxides are not so easy to obtain. After many kinds of aminoalcohol ligands were investigated, monomeric SCBA-1: Co[OCH(^{t}Bu)CH$_2$N(Et)(Me)]$_2$ was found to have the optimal vapor pressure (Figs.1 & 2).

ALD Co films grown with SCBA-1 will be also presented. Plasma-enhanced ALD (PEALD) was better to obtain pure Co metal films with low resistivity, though thermal ALD might be preferred for some applications. For future improvement, a strong co-reactant will be necessary for thermal ALD process using SCBA-1.

Reference: [1] ALD2018,S.Ivanov, [2] ALD2017, M.Kerrigan, [3] ALD2018, K.Väyrynen, [4] ALD2019, A.Nishida, [5] ALD2020, G.V.Straaten, [6] ALD2021, N.M.K.Linn, [7] ALD2012, T.J.Knisley

4:30pm AF-MoA-13 Expanding the tert-Butylimido Framework Beyond Molybdenum: New Refractory Metals and Ligands, *Kieran Lawford*, Carleton University, Canada*; M. Land,* Dalhousie University, Canada*; E. Goodwin,* Carleton University, Canada*; K. Robertson,* St. Mary's University, Canada*; S. Barry,* Carleton University, Canada

Refractory metals (Nb, Ta, Mo, W, Rh; sometimes V, Cr) and their alloys can be found in a variety of applications ranging from dry lubricants, rocket nozzles, surgical equipment, and as protective layers applied to cutting tools to improve cutting and reduces tool wear.[1] We have previously shown great success with incorporating *tert*-butylimido ligand frameworks into volatile molybdenum deposition precursors,[2] so we decided to explore the analogous Cr, W, V, Cr, Nb, and Ta compounds.[3] We prepared (^{t}BuN)$_2$MCl$_2$·**dad** (M = Cr, Mo, W, **dad** = 1,4-di-*tert*-butyl-1,3-diazabutadiene) by addition of **dad** to coordinatively unsaturated (^{t}BuN)$_2$MCl$_2$ compounds.[3] The ancillary **dad** ligand was chosen because it has previously been shown to yield a volatile and thermally stable scaffold in the Mo analogue.[2] Following an analogous protocol, the mono imido compounds, (^{t}BuN)MCl$_3$·dad (M = V, Nb, Ta), were also prepared.[3]

These compounds were fully characterized using common spectroscopic techniques including multinuclear NMR, FT-IR, and single-crystal X-ray diffraction.[3] The volatility of these compounds was measured using thermogravimetric analysis (TGA) and the V, Mo,[2] and W compounds exhibited good volatilities, with onsets of evaporation between 55 °C and 135 °C.[3] We also studied their thermal stabilities by differential scanning calorimetry (DSC) and observed they all undergo decomposition between 154 °C and 189 °C, suggesting similar decomposition pathways[3].

EI-HRMS suggests that these compounds decompose with their M≡N bond intact, so we decided to explore these compounds as vapour phase precursors of the corresponding metal nitrides. Preliminary deposition experiments showing that these precursors can be used for the single source CVD of MN$_x$films.[3] This presentation will further discuss preliminary ALD process development for the V, Mo, and tungsten compounds for the ALD of metal-nitride films on a homemade ALD tool.

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3. Lawford, K.; Land, M. A.; Goodwin, E.; Robertson, K. N.; Barry, S. T. Synthesis, Characterization, and Single-Crystal X-ray Structures of Refractory Metal Compounds as Precursors for the Single-Source Chemical Vapor Deposition of Metal Nitrides. *Inorg. Chem.***2023**, 62(*51*), 21061–21073.

4:45pm AF-MoA-14 Alkoxide Complexes as Precursors for Coinage Metal and Main Group Element Thermal ALD, *David Emslie,* Department of Chemistry, Canada*; M. Al Hareri, N. Hoffman,* McMaster University, Canada
Thermal ALD methods have been developed to deposit thin films of a wide range of materials. Methods to deposit metal oxides and metal nitrides are now well established, often involving reactions with O$_2$, O$_3$, H$_2$O or NH$_3$.[1] However, deposition of elemental metals[2-4] (or semimetals) can be particularly challenging, because it typically requires reduction of an element in a positive oxidation state in a precursor complex to the zero oxidation state in the metal (or semimetal) film. This reduction reactivity becomes increasingly challenging for more electropositive elements, and in ALD the choice of reductant (the co-reactant) is limited by the requirement for both the co-reactant and the reaction byproducts to be volatile and thermally stable. Furthermore, suitable choices of reducing co-reactant will depend strongly on the element to be deposited, the oxidation state of the

element in the precursor complex, and the ligands in the precursor complex.

This presentation will describe the development of novel thermal ALD methods to deposit coinage metal and main group elements using alkoxide precursors in combination with pinacolborane (HBpin). The envisioned chemistry involves exchange of hydride and alkoxide groups between the precursor and HBpin, where the driving force for film deposition is the formation of very strong B–O bonds, combined with eventual H$_2$ elimination. This work also includes the development of new coinage metal precursors, and a study of their volatility, thermal stability, and reactivity.

References

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5:00pm AF-MoA-15 Fluorinated Silver Alkoxides as Precursors for Atomic Layer Deposition, *Nick A. Hoffman, D. Emslie,* McMaster University, Canada
Elemental silver thin films are particularly desirable for photonic, electronic, catalytic, and biological applications.[i] Previously reported methods for thermal Ag ALD are scarce and suffer from poor film morphology.[ii] Additionally, the low thermal stability of Ag(I) precursors often necessitates delivery via direct liquid injection, adding complexities to reactor design.[iii] Herein we present the synthesis and characterization of a series of new fluorinated silver alkoxide complexes, an assessment of their thermal stability and volatility, and their application as precursors for thermal ALD of silver metal.

The fluorinated silver alkoxide complexes, [Ag{OC(CF$_3$)$_3$}(PR$_3$)]$_2$, are readily synthesized following a simple and scalable one-pot procedure. These compounds can be sublimed *in vacuo*, and thermogravimetric analysis (TGA) was conducted to evaluate their thermal properties. Solution-state reactions with various co-reactants yielded silver metal, suggesting a high degree of suitability towards novel thermal ALD processes. The precursor [Ag{OC(CF$_3$)$_3$}(P^{i}Pr$_3$)]$_2$ was selected as the most promising candidate for ALD, and was used to develop a new method for Ag thermal ALD.

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5:15pm AF-MoA-16 Atomic Layer Deposition of Niobium Carbonitride Thin Films, *Paloma Ruiz Kärkkäinen, T. Hatanpää, K. Mizohata, M. Putkonen, M. Ritala,* University of Helsinki, Finland
While the development of transition metal carbide (TMC) and, particularly, transition metal carbonitride ALD is still in its early stages, transition metal nitrides (TMNs) have numerous well-established processes. The high melting points, outstanding catalytic properties, chemical inertness, and tunable work functions of TMNs and TMCs offer great advantages over metal films while retaining excellent conductivity. The attractive properties of TMCs and TMNs arise from their unique structures, which combines

ionic, covalent, and metallic bonding. Their current and future applications include energy storage, quantum computing, low-cost catalysis, and in semiconductor device contacts, barrier-free interconnect materials and barriers themselves. Furthermore, they exhibit continuity at low film thicknesses, which remains a challenge for metal ALD.

In this work, we present for the first time ALD of NbC_xN_y films. Only a few metal carbonitride materials, such as WC_xN_y, TiC_xN_y, and TaC_xN_y, have previously been deposited with ALD.[1] The ALD of NbC_x is still relatively unexplored with only one process for an amorphous film.[2] We deposited NbC_xN_y films with NbF_5 and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine [$(Me_3Si)_2DHP$] at 200–450 °C. The films are crystalline as-deposited and the growth rate saturates to ~1.2 Å/cycle with respect to both precursors at 425 °C. The films show uniform resistivity (~150 μΩcm) across the 5 x 5 cm² substrates. We demonstrate process compatibility on a wide range of substrates, such as Si, TiN, and Mo.

TMCs and TMNs both consist of metal lattices with either C or N in the interstitial sites. Consequently, distinguishing carbide and nitride phases from carbonitrides with common characterization methods such as XRD and XPS is an extremely difficult task.[3] Aside from the challenge of determining which carbide and nitride phases the films consist of, the most demanding aspect is differentiating whether the films consist of separate NbC_x and NbN_y phases or NbC_xN_y. We will address the characterization challenges of carbonitrides by conducting extensive analysis with methods such as XRD, XPS, Raman, and ToF-ERDA. We will discuss tuning the properties, such as resistivity and morphology, as well as explore the superconductivity of the films to assess their potential for future applications.

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(3) Ruiz Kärkkäinen, P. et al. Atomic Layer Deposition of Molybdenum Carbide Thin Films. Manuscript submitted.

5:30pm AF-MoA-17 Using ALD Precursors as Inhibitors During Area-selective ALD, *Marc Merkx, P. Yu, S. van der Werf, A. de Jong, E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

In the pursuit to develop area-selective ALD processes with a high selectivity, the main question that needs to be answered is how to effectively block the adsorption of ALD precursors on the areas where deposition is not desired. One of the most studied instances of precursor blocking is self-limiting precursor adsorption during ALD, i.e., precursor adsorption is blocked when the surface is saturated by precursor adsorbates. To exploit this knowledge, the field of area-selective deposition is exploring the use of plasma-assisted ALD precursors (i.e. precursors that do not deposit material when exposed to a thermal co-reactant) as inhibitors for selective thermal ALD processes.[1,2] However, it can be expected that not all ALD precursors block precursor adsorption equally well. By studying the blocking mechanisms of ALD precursors against other precursor chemistries, important insight can be gained into how to design or select effective inhibitor molecules for area-selective ALD. In this contribution, we systematically study the blocking of ALD precursor adsorption by another ALD precursor molecule for a range of different precursor chemistries as a model system for precursor blocking.

To study the blocking efficiency of ALD precursors, a three step (i.e. ABC-type) ALD cycle was employed. During steps A and B, precursor 1 and precursor 2 are sequentially dosed, such that precursor 2 should be largely blocked by precursor 1. Finally, in step C, O_2 plasma is used as the co-reactant to remove all precursor ligands from the surface. The fraction of material that is deposited by precursor 2 in the resulting film was measured by x-ray photoelectron spectroscopy (XPS) and used as a metric for how effective precursor 1 can block precursor 2. Precursor blocking was studied for bis(diethylamino)silane (BDEAS), tetrakis(dimethylamino)titanium (TDMAT), tert-butylimidotris(dimethylamino)tantalum (TBTDMT), tris(dimethylamino)cyclopentadienylhafnium (HyALD), and trimethylaluminum (TMA). In general, it was observed that precursors that were effective at blocking precursor adsorption as precursor 1 were also difficult to be blocked when used as precursor 2, and vice versa. In addition, it was found that a CH_x termination is preferred over alkylamino termination for effective precursor blocking. In this contribution, the role that packing, reactivity, and ligand chemistry play in precursor blocking will be discussed.

[1] Soethoudt *et al.*, *J. Phys. Chem. C* **124**, 7163 (2020)

[2] Nguyen *et al.*, *Nat. Commun.* **13**, 7597 (2022)

ALD & ALE
Room Hall 5A - Session ALDALE-MoA

Student Awardees

Moderators: Annelies Delabie, IMEC, **Ivo Raaijmakers**, ASM

1:30pm ALDALE-MoA-1 ALD Student Award Finalist Talk: Gas Phase Deposition of ALF-MOF for Selective CO₂ Capture: A Molecular Layer Deposition Study, *Maram Bakiro, S. Barry,* Carleton University, Canada

The synthesis of alucones, a relatively new class of hybrid inorganic-organic materials, has traditionally been achieved via molecular layer deposition (MLD) using aluminum precursors like trimethylaluminum (TMA) and alcohol-functionalized organic ligands.[1] This method allows for consecutive self limiting gas deposition of organic-inorganic hybrid films with precise control over composition and structure. Alucones are particularly noted for their inherent porosity and low density, making them suitable for applications such as ultra-low-k dielectric films.[2]

Our research presents a novel adaptation of this established process, extending the utility of the alucone deposition technique to the realm of metal-organic frameworks (**MOFs**). Addressing the need for efficient carbon dioxide (**CO₂**) capture technologies, this study presents the pioneering the MLD of aluminum formate **MOF** (**ALF-MOFs**), which is traditionally synthesized via solvothermal methods and is known for its selectively capturing CO_2.[3] Using a commercial ALD tool (Picosun R200), ALF-MOF was deposited from the gas phase through a novel process involving TMA and formic acid (H_2CO_2), **Fig 1a**.

The growth-per-cycle (GPC) was 3.5 Å for **ALF-MOF**, (**Fig 1b and c)** which is characteristic of an alucone. Mass spectrometric analysis confirmed the polymeric nature of the film, highlighting the repeat unit $Al(OOCH)_3$. Further characterization through Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy) elucidated the bridging nature of the FA ligand to the Al nodes.

Quartz crystal microbalance analysis substantiated the step-wise growth of the target **ALF-MOF**. Additionally, the exposure of **ALF-MOF** to a CO_2/N_2 gas stream demonstrated its selective CO_2 capture capabilities. This presentation will delve into the nuances of the deposition and structure of ALF-MOF, emphasizing the nature and reversibility of CO_2 uptake. Our findings represent a significant advancement in MOF deposition, showing a scalable and efficient method for CO_2 capture that could have implications for environmental sustainability and industrial applications.

(1) Vemuri, V.; King, S. W.; Lanford, W. A.; Gaskins, J. T.; Hopkins, P. E.; Van Derslice, J.; Li, H.; Strandwitz, N. C. *Chem. Mater.* **2023**, *35* (5), 1916–1925.
(2) Dameron, A. A.; Seghete, D.; Burton, B. B.; Davidson, S. D.; Cavanagh, A. S.; Bertrand, J. A.; George, S. M. *Chem. Mater.* **2008**, *20* (10), 3315–3326.
(3) Evans, H. A.; Mullangi, D.; Deng, Z.; Wang, Y.; Peh, S. B.; Wei, F.; Wang, J.; Brown, C. M.; Zhao, D.; Canepa, P.; et al. *Sci. Adv.* **2022**, *8* (44).

1:45pm ALDALE-MoA-2 ALD Student Award Finalist Talk: Surface Functionalization of *Poly*-Si and SiO₂ Nongrowth Surfaces with Small Inhibitor Molecules to Enable Area-Selective Atomic Layer Deposition of Al₂O₃, *Andrew Kaye,* Colorado School of Mines, USA*; H. Chandra, R. Pearlstein, X. Lei, A. Derecskei, B. Zope,* Merck KGaA*; S. Agarwal,* Colorado School of Mines, USA

Poly-Si, SiO_2, and SiN_x are three commonly used films in semiconductor manufacturing, and area-selective ALD (AS-ALD) of dielectrics on these surfaces is desirable. In this presentation, we study the reaction mechanisms of small molecule inhibitors (SMIs) with *a*-Si:H, SiO_2, and SiN_x, using *in situ* attenuated total reflection FTIR spectroscopy. On each functionalized surface, we tested the ability of SMIs to prevent the growth of Al_2O_3 from dimethyl aluminum isopropoxide and H_2O using *in situ* IR spectroscopy and *in situ* 4-wavelength ellipsometry.

On an *a*-Si:H surface, our IR data shows that aldehydes [pivaldehyde, and 3,5,5-trimethylhexanal (TMH)] chemisorb onto surface –SiH_x groups to form alkoxides that are thermally stable up to ~250 °C (Fig. 1). The alkoxide formed after functionalization of *a*-Si:H with pivaldehyde is slightly more stable the alkoxide group obtained after functionalization with TMH (Fig. 1), most likely due to the absence of β hydrogen, which prevents the β-hydride elimination reaction — this limits the AS-ALD window to ~250 °C. We show that if the target growth surface is SiO_2, surface functionalization with aldehydes is selective to *a*-Si:H. If the target nongrowth surface is SiN_x,

aldehydes react with surface SiH_x groups to form alkoxides. Additionally, aldehydes also react with surface $-NH_x$ groups to form of aminoalcohols, enamines, and imines. Aminoalcohols are intermediates species and cannot be converted to imines by increasing the substrate temperature. The presence of aminoalcohols allows Al_2O_3 ALD precursors to bind to the functionalized SiN_x film, resulting in no nucleation delay.

Functionalization of SiO_2 with aminosilane SMIs has been previously reported,[1,2] but it is speculated that the presence of unreacted surface SiOH groups eventually leads to nucleation. The target growth surface in this case can be either *a*-Si:H or SiN_x. At elevated temperatures, the surface SiOH density decreases due to a H_2O condensation reaction between neighboring silicon hydroxides, leading to the formation of Si–O–Si bonds. We have studied the functionalization of SiO_2 with N,N-dimethylaminotrimethylsilane (DMATMS), which results in $-Si(CH_3)_3$ terminated surfaces. We have performed these surface functionalization experiments as a function of the pre-annealing temperature of SiO_2 to determine the optimal density of surface SiOH groups for adsorption of aminosilane SMIs (Fig. 2). Lastly, we will report the optimal surface coverage of SMIs for obtaining the highest degree of passivation for inhibiting Al_2O_3 ALD.

[1] Xu *et al.*, *Chem. Commun.* **58**, 6650 (2022)

[2] Xu *et al.*, *Langmuir* **30**, 652 (2022)

2:00pm ALDALE-MoA-3 ALE Student Award Finalist Talk: Precursor Mobility Through W Thin Films and sub-Surface Etching of Patterned TiO₂ *via* Atomic Layer Etching, *Hannah Margavio,* North Carolina State University*; N. Arellano, I. Singh, R. Wojtecki,* IBM Almaden Research Center*; G. Parsons,* North Carolina State University

Increasing complexity of nanoelectronic device architectures warrants novel atomic-scale fabrication methods. Current semiconductor processing of thin films involves distinct deposition and etch steps to achieve the desired device architecture. A key challenge, however, is to identify new process capabilities to expand synthesis of advanced materials with sub-nanometer features.[1] In this work, we describe a technique for removing thin films underneath a patterned surface in a process we term "sub-surface etching". It is known that during atomic layer etching (ALE) of thin films, a precursor converts the surface to a chemically distinct intermediate layer, and the second precursor volatilizes the conversion layer *via* ligand exchange.[2] This self-limiting mechanism assumes that: i) etching precursors remain on film surface, and ii) the entire intermediate layer undergoes volatile ligand exchange. In this work, we show that certain halogenated vapor-phase etching precursors can penetrate through thin films and react with underlying materials. To demonstrate reagent mobility through a thin film, we exposed TiO_2/Si line space patterns (shown in Figure 1a) to 10 W ALD cycles using 2% SiH_4 in Ar and WF_6 at 250 ºC. We have found that W metal deposition proceeds readily in the Si regions, and it is known that WF_6 spontaneously etches TiO_2 layers through the formation of $TiF_{4(g)}$ and $WF_2O_{2(g)}$.[2] The spontaneous etch process also leaves behind a thin layer of solid WO_xF_y on the TiO_2 surface, and we hypothesize that SiH_4 reduces the WO_xF_y layer through the formation of $SiF_{x(g)}$. A schematic of the resulting film stack is shown in Figure 1b. After 10 W ALD cycles, the resulting structure was exposed to 5 WF_6 and BCl_3 ALE cycles. The integrated 10 W ALD cycles and 5 WF_6 and BCl_3 ALE cycles deposits a 17 nm thick W layer and simultaneously etches the underlying TiO_2 feature. This process creates a uniform air gap between the etched TiO_2 and W overlayer, shown schematically in Figure 1c. We hypothesize that volatile species produced by the etch reaction diffuse out through the W overlayer. Depending on the relative WF_6 exposure, we have found the underlying TiO_2 may be partially or completely etched away. This process provides insights into the interactions between deposition and etching reaction mechanisms during integrated atomic layer process steps. More notably, this work gives a first example of vapor-phase, atomic-scale sub-surface etching and deposition, thus expanding the toolbox for thin film deposition and etching for sub-nanometer features.

[1] Clark, R. et al. *APL Mater*. **2018**, 6 (5)

[2] Lemaire, P. C.; Parsons, G. N. *Chem. Mater.* **2017**, *29* (16)

2:15pm ALDALE-MoA-4 ALD Student Award Finalist Talk: Unravelling the Role of Stoichiometry of ALD Nickel Cobalt Oxides on their Electrocatalytic Activity, *Renee van Limpt,* Eindhoven University of Technology, Netherlands*; M. Lao, M. Tsampas,* Dutch Insitute for Fundamental Energy Research (DIFFER), Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

Production of green hydrogen is a key contributor towards the development of a sustainable energy system, and the synthesis of platinum group metal-free oxygen evolution reaction (OER) electrocatalysts for H_2O splitting is presently subject of major investigation. Nickel cobalt oxides (NCOs) have attracted particular interest[1], especially spinel NCO, since it shows excellent stable electrocatalytic performance. Rock-salt NCO, on the other hand, is also promising due to its ability to convert to the OER-active hydroxide phase. Deployment of NCO electrocatalysts requires further understanding of their chemistry-crystal structure-OER activity relationship. To this purpose, the present work focuses on ALD NCO thin film model systems which are synthesized, characterized and subjected to extended electrochemical testing.

We have recently developed an ALD supercycle process based on cobalt cyclopentadienyl ($CoCp_2$) and nickel methylcyclopentadienyl ($Ni(^{Me}Cp)_2$) precursors and an oxygen plasma co-reactant[2]. ALD provides control over the chemical composition such that the phase transition from Ni-rich rock-salt films to Co-rich spinel films can be observed at ~55 at.% Co. The transition is accompanied by an increase in the +3-to-+2 oxidation state ratio of the metal centres. Electrochemical analysis in 1M KOH discloses a synergistic effect between Co and Ni metal centres, such that NCO films are more OER-active than Co_3O_4 and NiO. The OER activity of all films is driven by the formation of (oxy)hydroxide phase. Rock-salt films continuously form hydroxide phase during CV cycling, resulting in prolonged activation such that an optimal overpotential of 470 mV is observed for the 30 at.% Co film after 500 cycles. The presence of Co limits the bulk hydroxide formation, such that a constant performance at an overpotential of ~500 mV is observed for the spinel films. The activation process occurs in parallel with an increase in the electrochemical surface area (ECSA) up to a factor 8 for rock-salt films. The overpotential is corrected for this change in ECSA upon activation using an original approach. We conclude that Ni-rich spinel films are intrinsically the most OER active[3]. The improved OER-activity of rock-salt films upon electrochemical activation indicates that the low-cobalt content films (≤40 at.% Co) could be a sustainable alternative to the more commonly investigated cobalt-rich films.

[1] Gebreslase *et al.* J. Energy Chem. 2022, 67, 101-137

[2] van Limpt *et al.* JVSTA, 2023, 41, 032407

[3] van Limpt *et al.* ACS Catal. *under review*

2:30pm ALDALE-MoA-5 ALD Student Award Finalist Talk: First-Principles Screening of Precursor Reactivity for ALD of GeAsSe Thin Films for OTS Applications, *Bram van der Linden,* KU Leuven and IMEC, Belgium*; G. Pourtois, L. Nyns, A. Delabie,* IMEC, Belgium

Storage Class Memory (SCM) with ultrahigh capacity can be realized by three-dimensional stacking of memory cells that are enclosed by wires with perpendicular alignment. Selection of one cell in these three-dimensional arrays, however, does not only lead to a voltage in the activated cell, but also in neighbouring cells. To this end, the memory cells need to be accompanied by Ovonic Threshold Switching (OTS) materials which are amorphous chalcogenides that ensure selection of the desired cell only. Atomic Layer Deposition (ALD) is essential to realize conformal OTS films on three-dimensional structures with high aspect ratios. GeAsSe is a promising OTS material, although it remains challenging to establish an ALD process with high composition control. It is therefore important to identify precursors with sufficient reactivity, which is experimentally difficult because of the many possible precursor combinations for ternary materials. We therefore employed ab initio energy calculations under the assumption of gas-phase reactions. We studied the reactivity of 13 germanium, 8 arsenic and 9 selenium precursors, amounting to more than 900 precursor combinations. Each precursor contained one of the following functional groups: alkoxy, alkyl, alkylsilyl, amine, chlorine or hydrogen.

First, successful ALD precursor combinations from the ALD AtomicLimits database and other literature were confirmed. Second, the most favourable precursor combination of all was $As(NMe_2)_3$ with $HGeCl_3$. This combination outperforms the germanium-arsenic precursor combination from literature ($AsCl_3$ with $HGeCl_3$) and both precursors show sufficient reactivity with the commonly used selenium precursor $Se(SiMe_3)_2$. Third, $Se(SnMe_3)_2$ was unreactive with most of the co-reactants and could therefore serve as a potential inhibitor for area-selective ALD. Fourth, inclusion of both

hydrogen and chlorine instead of either one could help to improve the reactivity. Lastly, germanium and arsenic precursors with the same type of functional groups show strikingly similar reactivity trends with the selenium co-reactants. These insights could help the precursor design for thin films that comprise GeAs, GeSe or GeAsSe.

2:45pm ALDALE-MoA-6 ALE Student Award Finalist Talk: Investigating Patterning of MgZnO by Atomic Layer Etch mode, used For Compute and Memory Applications, *Leila Ghorbani,* KU Leuven and Imec, Belgium*; S. Kundu,* IMEC, Belgium*; S. De Gendt,* KU Leuven and Imec, Belgium

Magnesium Zinc Oxide (MgZnO) emerges as a promising metal oxide for advanced memory applications due to its ability to provide thermal stability and high electron mobility > 40 cm^2/VS while retaining the excellent electronic properties of pure ZnO [1]. Therefore, MgZnO finds potential applications in dynamic random-access memory (DRAM) and resistive random-access memory (RRAM) [2]. MgZnO is poised to play a crucial role in the development of electrical nanoscale devices and its patterning becomes a key challenge.

This study focuses on minimizing the chemical and physical damage occurring during the patterning process. This is crucial for preserving the carrier transport properties in these MgZnO-based thin films which in turn can impact device performance [3]. In response, we explore atomic layer etching (ALE) as a precision etching method [4] to mitigate these challenges.

The investigation involves understanding the etching mechanism in a 10 nm MgZnO film in both as-deposited state and as patterned structures using ALE mode. Initial experiments demonstrate that using Cl$_2$/CH$_4$ mixture in the adsorption step and Ar gas in the desorption step separately does not etch MgZnO. And we are able to establish an ALE window for MgZnO by combining these steps (Fig.1 a). The process reveals a controllable etching mechanism; however, the etching rate of Zn is found to be higher than that of Mg. Their respective etching mechanisms are predominantly chemical and physical for Zn, and mostly physical for Mg.

The ALE window is successfully transferred to patterned structures (pillars/spaces) with critical dimensions (CD) of 25 nm and a pitch of 90 nm. Transmission electron microscopy (TEM) (Fig.1 b) and energy-dispersive X-ray spectroscopy (EDS) results confirm minimal Mg residues between trenches and the presence of stable MgZnO composition under the hard mask (HM) used for patterning this thin layer. Half of the initial HM budget remains after etching, with reduced unwanted redeposition on the sidewalls.

This study presents a high-density demonstration of MgZnO patterning using ALE, showcasing the potential for further feature shrinkage and increased feature densities. To our knowledge, this work represents a significant achievement in the controlled patterning of MgZnO for advanced memory applications.

References

[1] Y. Li, et al. Phys. Status Solidi A, 219, (2022) 2200313.

[2] J. Hwang, et al. Materials Science and Engineering: B, 266 (2021) 115063.

[3] M. Geiger, et al. Advanced material interfaces, 7(10) (2020) 1902145.

[4] K. J. Kanarik, et al. J. Vac. Sci. Technol. A, 33(2), (2015) 020802.

3:00pm ALDALE-MoA-7 ALD Student Award Finalist Talk: In-situ FTIR Study of Oxygen Source Mixing for Hafnium Oxide Atomic Layer Deposition on Titanium Nitride, *Jin-Hyun Kim,* D. Le, M. Lee, T. Chu, D. Kim, J. Veyan, University of Texas at Dallas*; M. Benham, J. Spiegelman,* RASIRC*; S. Kim,* Kangwon University, Republic of Korea*; J. Kim,* University of Texas at Dallas

Doped hafnia is a promising material for memory applications due to its favorable ferroelectric characteristics. However, despite advanced HfO$_2$ ALD technology, hafnia-based ferroelectric devices continue to face challenges such as relaxation, imprint, fatigue, and breakdown.[1] Issues are linked to the interface conditions of the ferroelectric film to the electrodes. The problem worsens when the ferroelectric thickness is less than 5 nm, increasing series capacitance and hindering crystallization due to increased surface energy.[2] Therefore, enhancing the reliability and scalability of hafnia-based ferroelectrics requires understanding and optimizing the interface properties. One major source of oxygen at the oxide interface formation is the oxidation agent from the ALD process. Therefore, to minimize the formation of interfaces, the adoption of oxygen sources with a high oxidation potential is avoided. Conversely, weaker oxidants may insufficiently remove precursor ligands and other impurities, leaving contaminants that degrade the oxide film properties. This study introduces

oxidant mixing as a strategy to deposit high-quality oxide films while limiting interface formation.

Employing in-situ reflectance absorption infrared spectroscopy (RAIRS), this research investigates the impact of oxidant source mixing on the surface reaction mechanism and interfacial layer. Our previous studies of HfO$_2$ ALD with TEMA-Hf and H$_2$O, O$_3$, and anhydrous H$_2$O$_2$ on TiN substrate at 250°C revealed surface reactions of these oxidants.[3] O$_3$ exposure led to a continuous increase in Ti-O and TiN-O features, while H$_2$O and H$_2$O$_2$ facilitated the formation of self-limiting hydroxyl and hydroperoxyl groups on the TiN surface, effectively suppressing interfacial formation and enhancing film properties and reliability for H$_2$O$_2$-based capacitors. To investigate the effect of oxidant mixture, anhydrous H$_2$O$_2$ and a mixture with H$_2$O were exposed to the TDMA-Hf surface. A much milder reaction was observed using mixed H$_2$O$_2$, forming methoxy and hydroperoxyl bonds. This mild reaction indicates that surface reactivity can be controlled during ALD by adjusting the ratio of the oxygen sources. The surface reaction, material, and electrical properties of HfO$_2$ ALD and films deposited using mixed oxidants will be shown.

This work was supported by GRC-LMD program (task#3001.001) through SRC. We thank YEST and KEIT for supporting the project through ISTD Program (No.20010806). The BRUTE peroxide was provided by RASIRC, and the ozone generator by TMEIC.

[1] J. Mohan *et al.,ACS AELM*, 4, 4 (2022).

[2] H. Lee et al., ACS AMI, 13 (2021).

[3] J. Kim et al., ALD 2023.

3:15pm ALDALE-MoA-8 ALD Student Award Finalist Talk: A New Low Temperature ALD Process for Magnesium Oxide, *Florian Preischel,* D. Rogalla, A. Devi, Ruhr University Bochum, Germany

Based on its outstanding secondary electron emission coefficient (SEEC) of up to 15 as a thin film, Magnesium (II) oxide (MgO) is emerging as an efficient SEE material for optoelectronic applications.[1,2] Additionally, the non-toxicity and biocompatibility of MgO[3,4] enable its use as a protective gas-barrier layer on food packaging, for the encapsulation of pharmaceuticals and owing to its antibacterial properties it also appealing for the coating of medical implants.[5]

To transition these applications from research to industrial applications, it is necessary to develop scalable processes that enable the deposition of high-quality, defect-free MgO films. Specifically, SEE layers and the coating of (heat-)sensitive substrates necessitate mild, low-energy coating methods.[2,6,7] Owing to its self-limiting nature, ALD emerges as the most promising solution that offers a precise control over the thickness and morphology. Yet, ALD strongly relies on the underlying chemistry and the development of low-temperature thermal processes for MgO is currently restricted by the availability of suitable Mg precursors. Existing precursors are limited to compounds of the cyclopentadiene and β-diketonate type that require elevated temperatures or harsh co-reactants.[8,9]

Addressing this challenge, we herein introduce bis-(dimethylamino)propyl magnesium (II), [Mg(DMP)$_2$] that was designed to be thermally stable, yet highly volatile and reactive to facilitate low-temperature thermal ALD of MgO. The thermal properties of [Mg(DMP)$_2$] were evaluated by thermogravimetric analysis (TGA), revealing a high volatility and indicating its potential as an ALD precursor for MgO. Subsequentially, we developed a thermal ALD process for MgO with [Mg(DMP)$_2$] and water in a broad temperature range from 40 °C to 260 °C on Si substrates. ALD characteristics of saturation and linear growth were demonstrated with high GPC values of 1.91 Å at 120 °C and 2.40 Å at 40 °C (**Figure 1**, left), indicative for efficient surface reactions. The purity and stoichiometry of the resulting films, confirmed by RBS/NRA (**Figure 1**, right), underlines the potential of this approach for emerging MgO applications. By identifying a new and promising Mg precursor and an ALD process that can operate close to room temperature, including coating on polymer substrates, we advance the utilization of MgO thin films for new applications based on its unique properties.

Atomic Layer Etching
Room Hall 3F - Session ALE-MoA

ALD+ALE and Emerging Topics in ALE

Moderators: Robert Clark, TEL Technology Center, America, LLC, **Dmitry Suyatin**, AlixLabs A.B.

4:00pm **ALE-MoA-11 Highly Selective Si Vertical Etching Enabled by Atomic-Level Process Utilizing SiCl₄ Plasma-Induced Selective Deposition**, *Miyako Matsui*, Hitachi, Ltd., Japan*; M. Miura, K. Kuwahara,* Hitachi High-Tech Corp., Japan **INVITED**

Although the physical limitation of CMOS scaling is approaching, the local cell size of logic devices has still been continuously shrinking to improve the degree of integration. The patterning technology using extreme ultraviolet (EUV) lithography is one of key technologies for boosting pitch scaling. In addition, design technology co-optimization (DTCO) is another technology to boost cell size scaling, which enhances scaling by introducing various self-aligned processes. However, process challenges exist for both technologies. Etching processes using thin EUV resists, which needs to be thinner to accommodate the decrease in the depth of focus of EUV lithography, require extremely high selectivity and precise control of critical dimensions. Selective etchings for DTCO require high selectivity between layers having a similar material composition. In both cases, selective deposition for forming protective layers only on unetched materials can solve these process challenges and achieve extremely highly selective etchings.

In this study, we investigated a plasma-induced selective deposition process using a microwave-ECR etching system for forming a protective layer on top of the mask. A deposition layer was formed only on SiO_2 masks without forming an unnecessary deposition layer on Si surfaces of etching area, such as bottoms of the patterns and isolated etching area. This process effectively achieves extremely highly selective etchings by selectively forming the protective layers prior to the etching procedure in the same chamber.

We suggested a process for selectively forming protective layers on a SiO_2 without forming on a Si etching area by using a $SiCl_4/H_2/Cl_2$ plasma. On the Si surface, adsorbed $SiCl_x$ easily desorbed again by reacting with Cl generated from the plasma. On the other hand, adsorbed $SiCl_x$ on SiO_2 was thought to be more difficult to desorb by reacting with Cl due to Si-O having larger binding energy than Si-Si. After the deposition layer was selectively formed on the SiO_2 mask, the layer was oxidized using an O_2 plasma treatment to improve the etching resistance during the Si-etching. The O_2 plasma treatment time was controlled not to prevent the Si substrate from being etched during the Si-etching.

Finally, we demonstrated the selective deposition to etch a line-and-space pattern with a SiO_2 mask. In this process, selective deposition, oxidation, and Si etching were cyclically carried out. The extremely highly selective etching was achieved using the atomic-level selective deposition process without forming an unnecessary deposition on an isolated Si area.

4:30pm **ALE-MoA-13 Quasi-ALE Process Transfer from Lab to 300mm Line and Its Optimisation**, *Jenefa Kannan, M. Rudolph,* Fraunhofer IPMS-CNT, Germany*; R. Jam, A. Karimi, D. Suyatin, J. Sundqvist,* AlixLabs, Sweden

Atomic layer etching (ALE) has found its place in advancing technologies as chip sizes continue to shrink and pitch sizes get smaller. The ALE process offers several advantages over conventional reactive ion etching (RIE) such as better directionality, uniformity, selectivity and damage free surface after etching [1,2]. A self-limited removal of material with minimal damage to the surface requires a good control over every step of the ALE process [3]. Quasi atomic layer etching (QALE) is defined as a process when more than one mono-layer of the material is etched per cycle. Surface treatment, Control of ion energies and appropriate evacuation of the chemical component (Cl_2) is necessary to control the etch rate per cycle and achieve etch saturation in a cycle sweep.

In our work, we have conducted in-depth studies to set up a molecular QALE process as seen in Figure 1 at our 300 mm facility in an inductively coupled plasma (ICP); decoupled plasma source (DPS) AMAT chamber on 350 nm amorphous Silicon (aSi) which was deposited on 12" blanket wafers. First, experiments were conducted to establish the bias power and pressure window. After this step, Ar sputter threshold for amorphous Silicon was determined. This was used as baseline to setup a cyclic process where the EPC was determined over low ion energies by optimising the bias power and activation time during exposure to Ar plasma. Damage or roughness caused to the layer being etched severely degrades device

performance with decreasing dimensions [4]. Hence, to investigate the same, an Ellipsometer model was developed to understand the composition and thickness of this rough layer of the aSi surface post QALE etch. Thickness of the rough layer was evaluated over increasing number of cycles. The EPC for different Ar activation times at bias power 25 W is shown in Figure 2. The thickness of the rough layer at the end of the cycles is seen in Figure 3. We observed that the Ar activation time and no. of cycles have an influence on the thickness of the rough layer after etching.

In this work we investigate the factors and challenges that need to be taken into consideration while transferring the ALE process from lab to fab.In general, our work highlights the importance of control of every step in QALE for effective transfer and commercial viability in a 300mm line.

4:45pm **ALE-MoA-14 Deposition and Etchback Approach for Ultrathin ZrO₂ Coatings on TiO₂/ZrO₂ Core/Shell Nanoparticles**, *J. Sempel, M. Kaariainen, T. Colleran,* University of Colorado at Boulder*; A. Lifschitz,* Meta Reality Labs*; Steven George,* University of Colorado at Boulder

Atomic layer deposition (ALD) and atomic layer etching (ALE) techniques were used to deposit and etchback a thin ZrO_2 shell on TiO_2/ZrO_2 core/shell nanoparticles. Possible pinholes in the initial ZrO_2 shell on the TiO_2/ZrO_2 core/shell nanoparticles were minimized by first growing thicker ZrO_2 films by ZrO_2 ALD. These thicker ZrO_2 ALD films were then etched back to produce thinner more continuous ZrO_2 films. The ALD and ALE were performed while the nanoparticles were agitated using a rotary reactor. ZrO_2 ALD films were deposited using sequential, self-limiting exposures of tetrakis(dimethylamino) zirconium (TDMAZ) and H_2O. Self-limiting conditions for the ZrO_2 ALD were determined by monitoring the pressure during multiple micropulses of the ALD reactants. *Ex situ* analysis of the nanoparticles was performed using transmission electron microscopy (TEM) to observe the growth of the ZrO_2 shell on the core/shell TiO_2/ZrO_2 nanoparticles. The ZrO_2 ALD led to more spherical ZrO_2 shells on the crystalline and more irregular TiO_2 cores in the absence of nanoparticle aggregation. The ZrO_2 ALD on the nanoparticles had a growth rate of 1.1 Å/cycle. Tunable ZrO_2 coatings were observed with thicknesses ranging from 5 nm to 25 nm after up to 250 ZrO_2 ALD cycles. The ZrO_2 deposited film was then etched back using sequential HF and $TiCl_4$ exposures. Self-limiting conditions for the ZrO_2 ALE were again determined by monitoring the pressure during multiple micropulses of the ALE reactants. Quadrupole mass spectrometry (QMS) experiments also identified $ZrCl_4$ etch products and TiF_xCl_y ligand-exchange products during the $TiCl_4$ exposures. *Ex situ* TEM studies revealed that the spherical ZrO_2 shells were maintained during the ZrO_2 ALE with no observable nanoparticle aggregation. The ZrO_2 ALE on the nanoparticles had an etch rate of 6.5 Å/cycle. Tunable ZrO_2 coatings were produced by the ZrO_2 ALE from 25 nm back down to 5 nm using 30 ZrO_2 ALE cycles. This procedure employing ZrO_2 ALD and ZrO_2 ALE provides exceptional control over the ZrO_2 shell thickness and quality on the TiO_2/ZrO_2 core/shell nanoparticles.

5:00pm **ALE-MoA-15 Study of Depositing Si₃N₄ on Si Wafers Using PEALD and Atomic Scale Removal of Underlying Native Oxide Using PAALE in the Same Chamber Without Ion Bombardment Damage**, *Birol Kuyel, A. Alphonse, J. Alex,* Nano-Master

The mitigation of substrate damage is crucial to any process at the atomic scale (1). This is especially true for device technology applications in which source/drain and metalized regions are susceptible to damage (2). To eliminate substrate damage, we have developed plasma-enhanced atomic layer deposition (PEALD) of silicon nitride without ion bombardment (3).

The removal of native oxide on the Si wafer before depositing Si_3N_4 is also important for device performance (4). Removing the native oxides from the Si wafer using other means, such as reactive ion etching or wet etching, results in substrate damage and defects to the wafer.

Here, we will discuss the means of removing the native oxide from the Si wafer surface using Plasma Assisted Atomic Layer Etching (PAALE) prior to depositing silicon nitride. The PAALE process occurs in the same PEALD chamber, which prevents re-oxidation between steps. Furthermore, studies will be presented on the prevention of ion flux damage on the substrate surface with controlled ion energies and the possibility of performing PAALE without the incidence of any ions. The objective of the study is to develop a tool that can perform angstrom-precise PEALD and PAALE processes in the same chamber and prevent substrate damage.

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5:15pm ALE-MoA-16 N-Heterocyclic Carbenes for Area Selective Atomic Smoothing, *Eden Goodwin*, Carleton University, Canada; *M. Davies, P. Ragogna, M. Karttunen,* Western University, Canada; *S. Barry,* Carleton University, Canada; *C. Crudden,* Carbon To Metal Coating Institute / Queens University, Canada

High-volume manufacturing of microelectronics relies on thousands of sequential patterning, deposition, etch, and surface smoothing steps to create integrated circuits comprised of interwoven metallic, semiconducting, and dielectric features. Throughout the fabrication process, surface roughness is carefully monitored to ensure proper adhesion between layers and maximize distance between features. If surface roughness exceed tolerance limits, films are more likely to delaminate and manufactured features are more like to short-circuit.[1] At sub-nm feature sizes these tolerances become more challenging to reach.

Current smoothing techniques either rely upon top-down mechanical polishing[2] or on plasma methods.[3] Both techniques preferentially etch surface features, leaving a process gap for targeted surface smoothing on complex architectures. In pursuit of a more accessible smoothing methods compatible with complex architectures, we have identified a vapor phase method for smoothing gold surfaces using a known area selective small molecule inhibitor.[4] We explore the kinetics of adsorption and desorption of a N-heterocyclic carbene (NHC) through in-situ quartz crystal microbalance (QCM) analysis and molecular dynamics (MD) simulations. QCM traces (Fig. 1) show a saturative growth behavior for the initial dose of NHC achieving a surfactant density of 97 ng cm^{-2}, while subsequent doses saturate to 60 ng cm^{-2}. These differences are attributed to a reduction in the total number of available surface sites through atomic smoothing.

To confirm this, changes in surface roughness were analyzed through atomic force microscopy (AFM). AFM images (Fig.2) show a significant reduction in calculated root-mean-square (RMS) roughness values between surfaces left untreated (2.97 nm), heated under vacuum (2.38 nm) and those treated with NHC heated under vacuum (1.87 nm).

Area Selective ALD
Room Hall 3E - Session AS-MoA

Selective ALD by Area-Deactivation
Moderator: Stacey Bent, Stanford University

4:00pm AS-MoA-11 *Revealing New AS-ALD Chemistries with Ab Initio Approaches: From Interpretation to Prediction* , Ralf Tonner-Zech, Leipzig University, Germany **INVITED**

Area-selectivity is currently one of the key challenges in atomic layer deposition. The selectivity observed stems from different surface reactivities of precursors and - for inhibitor-based approaches - the inhibitor molecules. Ab initio approaches like density functional theory can help to reveal the key mechanisms underlying this selectivity. They thus help to understand experimental findings in the first step (interpretation). In the second step, theory can ideally provide design principles for inhibitors and precursors from detailed analysis of several systems (prediction). I will present our progress in both areas: (i) interpretation of new AS-ALD reactivities for small molecule inhibitor-(SMI-)based approaches to ALD on dielectric and metallic surfaces,[1] and (ii) understanding of design principles for SMIs and precursors using ab initio computations and electronic structure analysis.

[1] J. Yarbrough, F. Pieck, A. B. Shearer, P. Maue, R. Tonner-Zech, S. F. Bent, Chem. Mater.2023, 35, 5963–5974; (b) J. Yarbrough, F. Pieck, D. Grigjanis, I.-K. Oh, P. Maue, R. Tonner-Zech, S. F. Bent, Chem. Mater.2022, 34, 4646–4659; (c) S. Zoha, F. Pieck, B. Gu, R. Tonner-Zech, H.-B.-R. Lee, in revision.

4:30pm AS-MoA-13 Area Selective Atomic Layer Deposition Using a Size Cutter*, Han-Bo-Ram (Boram) Lee,* Incheon National University, Republic of Korea **INVITED**

Area-selective atomic layer deposition (AS-ALD) has received great attentions due to its potentials for a key toolbox in the nanofabrication of Si devices. The approach using inhibitor molecules which locally change surface chemical properties to inert toward the following ALD reactions has been widely used. The defect density of inhibitor layer which is a potential nucleation site should be minimized to achieve high selectivity, however, it is difficult due to the steric hindrance of inhibitor molecule during comparative adsorption. In this presentation, a simple approach to minimize the steric hindrance effects of inhibitor and maximize the blocking property is introduced. The ligand size of inhibitor layer could be reduced by only additional pulse of H_2O and the adsorption coverage of inhibitor could be increased. The concept of size cutter has been interpreted by using theoretical calculations with density functional theory (DFT) and Monte Carlo (MC) simulation and the results show highly consistency with experimental observation. The results could provide insights for the next generation nanofabrication in the semiconductor technology using AS-ALD.

5:00pm AS-MoA-15 ALD Young Investigator Award Finalist Talk: ALD Grown Self-Assembled Monolayers: Using Area-Selective Deposition to Characterize Molecular Scale Pinholes*, Sakari Lepikko,* R. Ras, Aalto University, Finland

Area selective atomic layer deposition has become a key method for creating patterned thin film structures for various applications in the semiconductor industry. Self-assembled monolayers (SAMs) are often used for de-activating surfaces, to block the ALD film growth (Figure 1). SAMs allow easy patterning, are capable of inhibiting wide variety of precursors, and are suitable on various substrates. Whereas certain SAM chemistries, such as alkyl trichlorosilanes are good for de-activating oxide substrates, they are also notoriously difficult to grow defect free, thereby reducing the SAM effectiveness to block ALD growth.

A promising option is to grow the SAMs directly in the ALD reactor, as it provides dry vacuum environment with good temperature control, thus making it an ideal tool for optimizing the SAM growth. Here, we present how the quality of non-fluorinated octyltrichlorosilane SAMs can be tuned to better block growth of various ALD films with differently sized precursor molecules [1]. By increasing SAM growth time its areal coverage increases, which leads to reduction of pinholes in the SAM and thus to the adsorption sites for the ALD reactant molecules (Figure 2). We also show that the maximal pinhole size reduces with the increasing coverage, which helps blocking adsorption of smaller ALD precursor molecules such as diethyl zinc. We see that growing SAMs directly in an ALD reactor could provide means to create more uniform SAMs with better resistivity against various ALD precursors, thus helping fabrication of even more demanding nanostructures in the semiconductor field.

We demonstrate that these SAMs have tunable hydrophobicity with extraordinarily low droplet friction. We demonstrate the world's most slippery surface by coating of SAM on black silicon.[1]

Lepikko, S., *et al.* Droplet slipperiness despite surface heterogeneity at molecular scale. *Nature Chemistry* (2024). https://doi.org/10.1038/s41557-023-01346-3

5:15pm AS-MoA-16 Area-Selective Etching of Poly(lactic acid) via Hydrogenolysis for Self-Aligned ALD*, Valtteri Lasonen, M. Ritala,* University of Helsinki, Finland

Our previous works have demonstrated that area-selective etching (ASE) of polymers is a novel approach for enabling self-aligned ALD.[1,2] In ASE, a polymer film is decomposed only on catalytic surfaces whereas on non-catalytic surfaces the polymer stays intact. ASE was demonstrated in the air using Pt as the catalytic and native SiO_2 as the non-catalytic surface with two polymers, polyimide and poly(methyl methacrylate) (PMMA). After the ASE of polyimide, ALD-Ir grew only on the exposed Pt surface, whereas no growth was observed on the polyimide. In the case of ASE of PMMA, small amount of ALD-Ni growth occurred also on PMMA. However, a simple lift-off after the ALD removed the unwanted Ni. Other catalytic surfaces were also identified, such as CeO_2 . Furthermore, it was demonstrated that only a small amount of ALD-Pt or ALD-CeO_2 , even down to a fraction of a monolayer, was enough to show a clear catalytic effect. This means that small amounts of Pt can be deposited on a metal surface, and CeO_2 on an insulator surface, to catalytically activate them. This is important because neither Pt nor CeO_2 is commonly used in semiconductor devices.

Many materials used in semiconductor devices are prone to oxidation when heated in the air, thus, non-oxidative atmospheres must be found for ASE. Two such atmospheres, inert (99.999% N_2) and H_2 (5% H_2 in Ar), were tested with PMMA and polyimide.[1,2] Out of all the surfaces tested only Ti, Pd, and Cu showed some catalytic effect in the inert atmosphere and/or in the presence of H_2. For example, the well-known hydrogenolysis catalyst, Pt, did not show any catalytic effect on the decomposition of PMMA in the presence of H_2. This is most likely because PMMA is not susceptible to hydrogenolysis, unlike condensation polymers, such as poly(lactic acid) (PLA). Here, we demonstrate that PLA is catalytically decomposed on several known hydrogenolysis catalysts, such as Pt, Ir, and Ni in the presence of H_2 whereas in the inert atmosphere PLA films stay intact on these surfaces at the same temperatures. Additionally, Co is demonstrated to work as a catalytic surface also in the inert atmosphere. In this case the removal mechanism is catalytic cracking of the polymer. These new findings give us confidence that ASE of polymers is possible with plethora of different surface combinations by carefully choosing the right catalytic material, polymer, and atmosphere, thus allowing new self-aligned ALD processes.

References

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2. Lasonen et al. *Chem. Mater*. **2023**,35(15), 6097–6108.

5:30pm **AS-MoA-17 Selective Surface Fluorination to Enable ASD of Polymer and Metal Oxide on SiN vs. SiO₂**, *Jeremy Thelven, H. Oh, H. Margavio, C. Oldham, G. Parsons,* North Carolina State University

3D integration of semiconductor devices such as Gate-All-Around FETs and vertical device stacking is being implemented to reduce power consumption and enable further scaling for logic and memory devices.[1] There is a critical need to reduce the processing budgets to achieve such advanced designs and area-selective deposition (ASD) offers a bottom-up approach to achieve the desired scaling goals.[2] The ability to selectively react and deposit on an oxide vs nitride surface is widely recognized as key roadblock for scaling due to the chemical similarity of these surfaces. ASD on nitride vs oxide surfaces, or vice versa will provide new options for patterning, to improve self-alignment, and to reduce edge placement errors. In this work, we demonstrate the use of a selective surface fluorination treatment to promote ASD on SiN vs. SiO_2.

To demonstrate ASD on SiN vs. SiO_2, we explored a surface treatment using molybdenum hexafluoride (MoF_6) on blanket SiN and SiO_2 wafers. Next, we deposited about 50nm of polypyrole (PPy) CVD on both surfaces. We found that PPy proceeded to grow as a film on the SiN surface after a brief nucleation delay, while only showing isolated nuclei on the fluorinated SiO_2 surface. As a further demonstration, experiments were performed on patterned SiO_2/SiN wafers which further confirmed PPy selective growth. We believe the MoF_6 exposure leads to the fluorination of both surfaces, which was confirmed by XPS, where this fluorination selectively passivates PPy growth on the SiO_2 surface. To extend this demonstration of ASD on SiN vs SiO_2 to other types of materials, we recently tested the treatment with the deposition of TiO_2 through ALD. We found that this selective fluorination passivation of the SiO_2 surface allows for selective growth of TiO_2 on SiN. The mechanisms behind selectivity, and the extent of passivation are currently under investigation by our group.

1 Datta, S.; Dutta, S.; Grisafe, B.; Smith, J.; Srinivasa, S.; Ye, H. Back-End-of-Line Compatible Transistors for Monolithic 3-D Integration. IEEE Micro 2019, 39 (6), 8–15. https://doi.org/10.1109/MM.2019.2942978.

2 Decadal Plan for Semiconductors. Semiconductor Research Corporation. https://www.src.org/about/decadal-plan/

Monday Evening, August 5, 2024

ALD Fundamentals
Room Hall 3 - Session AF-MoP

ALD Fundamentals Poster Session

AF-MoP-1 Depositing a Uniform Thin Film of Al₂O₃ Using Atomic Layer Deposition (ALD) onto 2D Electronics to Provide Protective Capping and Surface Passivation, *S. Lee, J. Lee, A. Cho, D. Ryu, **Hyunbin Chung**, K. Kim, T. Choi,* Sejong University, Republic of Korea

Our research focuses on the utilization of passivation layers in semiconductor products to shield materials from environmental degradation. These layers must demonstrate high chemical resistance and a low surface recombination rate to effectively protect the semiconductor surface. Aluminum oxide emerges as a suitable material for such layers due to its excellent chemical resistance, etch selectivity, density(2.5-3.8 g/cm³), and low dielectric constant(ranging between approximately 4 and 9). We investigate the properties of aluminum oxide through atomic layer deposition (ALD) parameter control and post-treatment methods like rapid thermal annealing (RTA) and UV treatment.

AF-MoP-2 Developments in Processing Large Area 2D Materials and Metals via ALD, *Nils Boysen, R. Neubieser,* Fraunhofer IMS, Germany; *F. Zimmermann, K. Brinkmann,* University of Wuppertal, Germany; *M. Michel,* Fraunhofer IMS, Germany; *T. Riedl,* University of Wuppertal, Germany; *A. Devi,* Ruhr University Bochum, Germany

ALD processing of 2D materials and metals are in great demand to realize next-generation devices with intricate structures and feature sizes in the nanometer regime. The joint research activities between RUB and IMS in collaboration with BUW have focused on the rational development of new precursors and ALD processes on chip- and wafer-level (8"). High quality materials such as MoS₂, WS₂, Ag, and Cu were realized among others, which are highly relevant for different micro- and optoelectronic applications.

The layered 2D materials MoS₂ and WS₂ possess unique functional properties which can be exploited for a variety of applications. In our recent studies, we have developed new MoS₂ and WS₂ ALD processes on 8" Si wafers with promising characteristics of the deposited materials. The thermally-driven ALD process with an amide-based Mo precursor [Mo(NMe₂)₄] and H₂S yielded MoS₂ layers at very low deposition temperature of 100 °C (Figure 1) on glass and Si/SiO₂ substrates. The resulting films exhibited promising gas-sensing behavior towards NO₂, NH₃ and H₂S.[1] At higher deposition temperatures (> 300 °C), crystalline WS₂ films on 8" Si wafers were deposited. This study not only demonstrates the scalability of MoS₂ and WS₂ on different substrates, but gives a perspective for the fabrication of advanced sensor structures in the future.

In another important field, we focused on the development of Cu and Ag precursors for spatial ALD (SALD) of the respective metals, which are especially important as electrode material for next-generation solar cells. We focused on Cu and Ag precursors based on carbenes that are specifically tailored to impart high thermal stability, while still possessing high reactivity. These new precursors enabled promising SALD processes in terms of very low deposition temperatures (60 °C) and high growth rates. These notable features prompted us to integrate the SALD Ag films in organic solar cells as an electrode material for the first time (Figure 2) displaying encouraging properties.[2]

In summary, the new and promising developments in terms of precursors and new ALD processes have prompted us to further explore the field of 2D materials and precious metals to make advancements in functional device applications.

AF-MoP-3 Sacrificial Copper Nitride Layer for PEALD of Copper, *Sakari Kettunen,* University of Helsinki, Finland; *M. Schalk,* Eindhoven University of Technology, Netherlands; *M. Chundak,* University of Helsinki, Ukraine; *M. Ritala, M. Putkonen,* University of Helsinki, Finland

Initial island formation during film deposition is well-known, although mostly unwanted behaviour while depositing thin metal films. This agglomeration is a result of the minimization of chemical potential, where coalescence with other metal atoms is preferred especially on silicon and metal oxide surfaces. While aiming to uniform sub 10 nm metal interconnect films selection of the substrate as well as tailoring interface layers have detrimental role.[1]

Cu₃N is considered an interesting seed layer for copper depositions, and it also offers indirect route to metallic copper thin films by annealing due to its low decomposition temperature of ~200 °C under H₂. It has also gained increased interest as catalyst as well as solar absorbing material. Cu₃N has been previously deposited by thermal ALD by using [Cu(ˢBuAMD)]₂[2], Cu(dmamb)₂[3] or Cu(hfac)₂[4]and ammonia at 100-190 °C, depending on the copper precursor used. Also PEALD has been utilised with Cu(hfac)₂ and NH₃ plasma for preparing nanocrystals at 150 °C.[5]

In this work Cu and Cu₃N thin films were deposited by PEALD using Cu(dmap)₂ as a metal precursor. Depositions were carried out by using Beneq TFS-200 either in direct or remote plasma set-up. Copper films were deposited while using Ar as carrier gas and H₂ as plasma gas. GPC of 0.21 Å/cycle and 0.37 Å/cycle were achieved in the remote and direct plasma configurations, respectively. Cu₃N was obtained by remote PEALD with GPC of 0.6 Å/cycle at 65 °C when the carrier gas was switched to N₂.

While depositing Cu/Cu₃N onto Si substrates it was observed that thin intermediate Cu₃N layer was converted to metallic Cu. According to XPS after removing surface contaminations by sputtering no N 1s signal were detected indicating Cu₃N conversion.

It was observed that to obtain conductive Cu films over 500 cycles (appr. ~11 nm when deposited by remote PEALD) were needed when using Cu(dmap)₂ + H₂ plasma process alone. By contrast, when starting with 75 Cu₃N cycles, already 175 Cu cycles deposited a continuous film with a thickness of 5.7 nm as measured by EDS.

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(3)J.-M. Park, et al. *Thin Solid Films***2014**, *556*, 434–439

(4)T. Törndahl, et al. *J. Electrochem. Soc.***2006**, *153* (3), C146

(5)L.-C. Wang, et al. *ACS Appl. Nano Mater.***2018**, *1* (7), 3673–3681

AF-MoP-4 Characteristics of Silicon Nitride Thin Films Deposited Using a Two-Step Plasma Enhanced ALD Process at Very High Frequencies, *DA EUN BAE, H. KIM,* CN1 Co., Ltd., Republic of Korea; *S. LEE,* DNF Co., Ltd., Republic of Korea; *J. CHOI, J. JEONG,* CN1 Co., Ltd., Republic of Korea

Despite its many advantages such as high step-coverage, atomic-level thickness control, and uniform film deposition, atomic layer deposition (ALD) processes have encountered difficulties in applications outside of semiconductor manufacturing due to their low deposition rates. Additionally, a high temperature (>400°C) process is required for high-quality properties when the thermal ALD is used for the deposition of nitride films such as SiNₓ, AlN, TiN, and TaN, leading to active development of the plasma-enhanced ALD (PE-ALD) processes and its precursor sources.

We have studied the characteristics of silicon nitride (SiNₓ) films deposited using a two-step PE-ALD process shown in Fig. 1 at low temperatures (≤200°C) and very high frequencies. Fig. 2 shows the NSi-01 precursor used as the silicon source. The two-step reaction uses NH₃ and N₂ plasma as reactants. The purposes of two-step PE-ALD are high deposition rates, low damage, and reduction of impurity contents. Electron temperature (Tₑ), ion flux, and ion density were monitored. Thickness and refractive index were measured using ellipsometry. Impurity content was measured through XPS depth profiling. Substrate damage due to plasma was examined by TEM.

AF-MoP-5 Analysis of ALD Thin Films by Combining MEIS and ERDA Techniques, *Aqsa Ashraf, K. Mizohata,* Helsinki Accelerator Laboratory, University of Helsinki, Finland; *M. Ritala,* HelsinkiALD, University of Helsinki, Finland

Thin film characterization in fast and reliable way is essential for the development of materials synthesis methods for present day and future applications. Requirement ofquantitative depth profiling with sub nanometer depth resolution atsurfaces and interfaces has pushed ion beam based analytical techniquesto their limits and extensive effort in developing new analyticaltechniques are required. Additional challenge in the analysis of thinfilms is light impurity elements, especially hydrogen. Ion beam-based materials characterization methods provide stand-alone solutions based on relatively simple kinematics and cross sections. Medium Energy Ion Scattering Spectroscopy (MEIS) has emerged as a powerful technique for

probing surface and near-surface structures with high precision and sensitivity.

MEIS with high resolution spectrometers hasincreasingly applied to analyze compositional depth profiles of a nano-scale thin films. However, MEIS has limitations in analysis of verylight elements in heavier matrix. To overcome these limitations, elasticrecoil detection analysis (ERDA)is used. During last decades The ERDA method has become one of thestandard techniques, especially for light element depth profiling ofthe thin films. However, ERDA depth resolution at the surface is orderof few nm in the surface region. In this work we present MEIS and ERDA setups for thin film analysis inUniversity of Helsinki.

Understanding the structural and compositional properties of ALD thin films is crucial for optimizing their performance. The present work concentrates on demonstrating benefits gained by thecombined use of ERDA and MEIS techniques in the analysis of thin ALD films. Combining these methods high depth resolution is achievable. This integrated approach not only provides a deeper understanding of ALD thin films but also paves the way for the development of innovative materials and devices with enhanced performance and functionality.Theadvantages and limits of this method are discussed in detail.

Keywords: MEIS, ERDA, Depth Profiling, Elemental Composition, Thin films

AF-MoP-6 Novel Liquid Lanthanide Precursors with Low Viscosity and High Volatility for Atomic Layer Deposition of Lanthanide Oxide Thin Films

Hanbyul Kim, SK Trichem, Republic of Korea*; H. Oh,* SK trichem, Republic of Korea*; B. Ryu, Y. Park,* SK Trichem, Republic of Korea

The necessity for highly conformal thin films of transition metals and metal oxides in various technological applications emphasizes the significance of lanthanide precursors. Lanthanide oxide films have many applications in catalysis and semiconductor devices. In this study, we investigated the properties of various Lanthanide precursors for semiconductor devices. Among them, Gadolinium oxide, well-known for its high dielectric constant, substantial band gap energy, elevated refractive index, and consistent thermodynamic stability at high temperatures, is under consideration for integration into CMOS devices, antireflective coatings on solar cells, and passivation layers for III-V semiconductors.[1]

Lanthanide oxide films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique since it gives Angstrom-level thickness control and can afford conformal coverage in high aspect ratio features. ALD precursors reported to date for Gadolinium oxide films have problems that most of these compounds have solid properties, and these solid precursors usually exhibit undesirably high melting points. Even in liquid phase, they are not suitable for ALD processes due to their high viscosity and low volatility characteristics.[2]

Herein, we developed various novel liquid lanthanide precursors (Gd, Sm, Dy, Ho, Yb, Lu) with low viscosity, good volatility and excellent thermal stability. The compounds were confirmed by NMR, and evaluated physical & chemical properties such as volatility, vapor rate, melting point, and vapor pressure, thermal stability and chemical reactivity. In this study, we anticipate that the newly developed Lanthanide precursor will be a promising candidate for ALD processes. It possesses properties suitable for application in next-generation semiconductor devices.

References

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AF-MoP-7 Novel Amidinate Ligand-based Scandium Precursor for Atomic Layer Deposition of Sc₂O₃ Thin Films

Hansol Oh, SK trichem, Republic of Korea*; H. Kim, B. Ryu,* SK Trichem, Republic of Korea*; W. Jeon,* Kyunghee University, Republic of Korea*; Y. Park,* SK Trichem, Republic of Korea

Scandium oxide (Sc_2O_3) thin films are essential for various applications due to their valuable intrinsic material properties and play a broad role in applications. Heat-resistance, high melting point, high optical transparance, high refractive index and laer-damage coatings. [1]

The high dielectric constant (high-*k*) and the large intrinsic bandgap(Eg = 6.0 eV) makes this helpful material as a high-k material for implementation as a potential gate dielectric in metal oxide semiconductor field effect transistors. [2]

Therefore, some of Sc precursor complexes have been reported; most of these compounds have solid properties, and these solid precursors usually exhibit undesirably high melting points. They have superior thermal stability but have the disadvantage of low vapor pressure. Furthermore, they are often bulky and suffer from low reactivity with oxidants. [3]

Herein, we developed a novel Amidinate ligand-based liquid scandium precursor with very low melting point, very low viscosity, good volatile and thermal stability to solve this problem. The thermal atomic layer deposition (ALD) of the newly designed scandium precursor has developed using ozone as an oxygen source. ALD growth behavior was observed for the growth of the Sc_2O_3 films within an ALD window of 300 to 320 °C on SiO_2 substrate and a growth per cycle (GPC) up to 0.065 nm/cycle at 300°C. The resulting Sc_2O_3 films possess a cubic phase crystalline structure while avoiding any carbon and nitrogen contamination. We fabricated Sc_2O_3 doped ZrO_2 capacitors with TiN electrode using ALD and evaluated their electrical properties such as dielectric constant and leakage current.

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[1] Thin Solid Films 368 (2000) 116–124.

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AF-MoP-8 Process Development of Cobalt Metal ALD on Novel ALD Machine

Mathias Franz, L. Kaßner, Fraunhofer ENAS, Germany*; C. Thurm,* University of Technnology Chemnitz, Germany*; L. Jäckel,* Fraunhofer ENAS, Center for Microtechnologies (ZfM), Chemnitz University of Technology, Germany*; M. Daniel,* scia Systems GmbH, Germany*; F. Stahr,* Forschungs- und Applikationslabor Plasmatechnik GmbH, Germany*; S. Schulz,* Fraunhofer ENAS, Center for Microtechnologies (ZfM), University of Technology Chemnitz, Germany

ALD of metallic films is a broad an ongoing topic of research. The conformal deposition of metallic cobalt is relevant for modern interconnects[1], seed layers for electroplating[2], and antibacterial coatings[3]. One of the essential process parameters is the deposition temperature. Especially low process temperatures enable depositions on substrates with a critical thermal budget. Here, we present the process development on the novel scia Atol 200 ALD reactor.

The process development was done on a *scia Atol 200* reactor, which was designed and fabricated by *scia Systems GmbH* in cooperation with *Fraunhofer ENAS*, the *Chemnitz University of Technology*, and *Forschungs- und Applikationslabor Plasmatechnik GmbH*. Figure 1 shows a photo of the ALD reactor. We integrated 2 CEMs, 2 Vapbox Systems, and 2 Bubblers as evaporation units. This provides the opportunity to use a wide range of precursors, including substances with low vapour pressure as well as high vapour pressure. The reactor design was accompanied by CFD fluid flow simulations. Figure 2 shows the precursor concentration on top of the wafer surface. The concentration deviation is less than ±10 %. The process development was done using $[Co_2(CO)_6(HC{\equiv}CC_5H_{11})]$ as precursor. The synthesis was reported earlier by Georgi et al.[4]. The processes took place on standardised 200 mm Si wafers with a preliminary 100 nm SiO_2 layer. We could show that all three types of evaporators were suitable to bring this cobalt complex into the gas phase. The following results are based on evaporations using a bubbler with Ar carrier gas. A full ALD cycle consists of precursor pulse, Ar purge, H_2 plasma pulse, and a second Ar purge. The deposited cobalt films were analysed by *in-vacuo* ellipsometry to determine in-line the film growth rates. Figure 2 shows the growth rates in the temperature range from 35 °C to 125 °C showing the ALD window for this process within the range of 50 °C to 110 °C.[5] The process was optimised regarding pulse and purge duration times to ensure stable saturation conditions. *Ex situ* measurements with XPS confirm that cobalt is in metallic state.

We demonstrated the successful development of the scia Atol 200 ALD system with a low temperature ALD process for metallic cobalt.

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Monday Evening, August 5, 2024

AF-MoP-9 High Quality TiN Plasma Enhanced Atomic Layer Deposition on SiO₂ Substrate with AlN Interfacial Layer via in situ Atomic Layer Annealing, *Valentina Korchnoy,* Technion Israel Institute of Technology, Israel*; I. Popov,* The Hebrew University of Jerusalem, Israel*; M. Koifman Khristosov,* Technion Israel Institute of Technology, Israel*; M. Lisiansky,* Tower Semiconductor, Israel

TiN layer becomes an important electrode material for devices with complex 3D geometry due to its scalability, compatibility with CMOS technology and low resistivity. The resistivity of thin TiN films depends on many factors, among them crystalline morphology of the film plays a dominant role. There are several factors determining the crystalline properties of TiN films deposited by PEALD. As was shown in [1] the crystallinity of the underlying substrate is an important factor influencing the grain size of a thin TiN PEALD film, and thus, its resistivity. There is few knowledge about the role of the interfacial layer (IL) on structural properties of thin polycrystalline TiN films grown by ALD on amorphous substrate. Crystalline properties of the IL, primarily, lattice matching to on-grown TiN layer and the ability of IL to be introduced in the advanced technology processes are the dominant factors that should be considered. PEALD AlN film as the IL satisfies both these requests. Another factor that promotes crystallinity of AlN PEALD film is the atomic layer annealing (ALA). It supplies an additional energy to the deposition process, stimulates surface reactions, increases the metal adatoms mobility, and thus promotes densification of the deposited film [2].

The purpose of this work was to investigate the effect of AlN IL and ALA technique on the crystalline properties of very thin (~ 14 nm) TiN layers deposited on Si/SiO₂ substrate.

The AlN and TiN layers were deposited on 100 Å thermal oxide layer grown on (001) Si substrate. The deposition was done by PEALD, using either N₂ or NH₃ plasma, by applying layer-by-layer, in situ ALA treatment using Ar plasma in each ALD cycle (FIG.1). The reference TiN samples were grown on the crystalline substrate (sapphire), that enables an excellent matching of AlN IL to the substrate. The reference samples provide data about TiN film grown at perfect conditions.

The study was conducted using numerous analysis techniques (TEM, EELS, STEM, XRD, XRR, AFM) and electrical characterization. The electrical resistivity of TiN films was measured using four-point probe Kelvin structure. The attached Figures 2,3,4,5,6,7 and Table 1 demonstrate the structural and electrical characteristics of 14 nm TiN layer. The lowest known resistivity of 70 µΩ·cm on the amorphous, and 10 µΩ·cm on the crystalline substrates were measured. The postdeposition annealing didn't cause significant resistivity change. According to XRR, the densities of the deposited thin AlN and TiN films are close to the bulk densities of these materials. Discussion about the conductivity mechanism in thin TiN layers was considered.

AF-MoP-10 Turning Online ALD and ALE Databases Into AI-Ready Tools for Development of New Sustainable Materials and Fabrication Processes, *Adrie Mackus,* B. Macco, Eindhoven University of Technology, Netherlands*; B. Karasulu,* University of Warwick, UK*; J. D'Souza, S. Auer,* L3S Research Center at Leibniz University of Hannover, Germany*; E. Kessels,* Eindhoven University of Technology, Netherlands

Artificial Intelligence (AI) presents unmatched opportunities to enhance ALD and ALE process development, not just by optimizing efficiency and reducing costs, but notably by driving innovation through data analysis, predictive modeling, and automation. However, the advancement of AI-based process development and material synthesis requires databases with extensive training data as input. Building on popular crowd-sourced databases containing ALD (DOI: 0.6100/alddatabase [https://www.atomiclimits.com/alddatabase/]) and ALE (DOI:10.6100/aledatabase [https://www.atomiclimits.com/aledatabase/]) process details as launched by TU/e on www.AtomicLimits.com in 2019, we have set up a program to start making these databases AI-ready. With this, we aim also to explore new opportunities for AI-inspired process development, materials design and autonomous experimentation. Bringing together three parties with complementary expertise, the program will focus on: defining integrated workflows and protocols for AI-aware ALD/E experiments and atomic-level simulation, coupled with the implementation of FAIR principles and neural language model-based knowledge extraction. We believe that the open-domain ALD/E databases resulting from this pilot will enable the AI-driven design of material stacks for highly-scaled devices, thereby reducing material usage and leading to overall more sustainable semiconductor fabrication processes. By sharing the protocols with the atomic-scale processing community, we hope to create a culture of AI-aware experimentation and simulation.

AF-MoP-11 ALD Process Characterization, Development, and Monitoring Using an Electron Impact Time-of-Flight Mass Spectrometer, *Abdelhak Bensaoula,* C. De Koning, C. Frege, TOFWERK, Switzerland*; T. Nelis,* BFH, Switzerland*; C. Hain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Guerra,* Swiss Cluster, Switzerland

Time of Flight Mass spectrometry (TOFMS) applications extend beyond materials science and technology and include industries spanning automotive, metallurgy, biotechnology, pharmaceutical, aerospace, etc. These mass spectrometers can be equipped with an electron impact (EI) source to measure neutral species, but the inlet stage can be designed to allow for (process) ionized species to be directly detected as well. Current TOFMS capabilities fulfil requirements of most industrial use-cases but the trend in advanced processes is to utilize energetic species to further enhance the manufacturing method. It is thus desirable to measure both the abundance of the neutral species but also that of the native ions. We present here a new member of the TOFMS instruments which allows just that.

The pgaTOF, an EI-TOFMS by TOFWERK, allows full m/q spectra acquisition at >1 kHz, up to 8000 mass resolution and 5 ppm mass accuracy, 10^6 dynamic range and a nominal mass range of >1000 Th. Thanks to an integrated filtering feature, our instrument allows for reduction/suppression of up to four user-selected masses which permits measurement of both main and trace compounds and avoids detector saturation and degradation issues. This feature is essential in ALD where precursor and purge masses signals are high while that of the reaction products are much smaller. The new instrument extends the EI-TOFMS capabilities to measuring native ions, such as those present in plasma-enhanced ALD. In our experiments, the TOFMS instruments were attached to various ALD reactors running different chemistries (Al, Cu, Li, etc.).

We will first present details of the EI-TOFMS instruments and its time resolution and sensitivity capabilities. We will then give examples of ALD results showing how real-time ALD process monitoring not only permits unique insights into the ALD chemistries, allows for significant time savings in recipes development but also determines excursions beyond the ALD mode or equipment malfunctions.

AF-MoP-12 Tailoring Cobalt Precursors Through Molecular Engineering, *Jean-Pierre Glauber,* J. Obenlüneschloß, D. Zanders, Ruhr University Bochum, Germany*; S. Barry,* Carleton University, Canada*; A. Devi,* Ruhr University Bochum, Germany

Cobalt based materials are indispensable for numerous applications due to their appealing physical and chemical properties. Their scope of application ranges from integrated circuits (IC) over electrocatalysis to spintronics. Metallic cobalt is promising as interconnects in IC devices.[1] While cobalt oxides are highly efficient for the oxygen evolution reaction (OER),[2] the Weyl-semimetal cobalt disulfide (CoS_2) is interesting for spin-to-charge conversions in the emerging field of advanced spintronic devices.[3] Such targeted applications require a synthesis route that allows film growth with precise thickness control on complex geometries. Atomic layer deposition (ALD) is the method of choice when it comes to meeting these demands and one crucial parameter is the precursor choice as its physiochemical properties directly influences the ALD process characteristics. Surprisingly, in the literature, the class of all-nitrogen coordinated cobalt precursors is rather underexplored.

With our goal to expand the library of Co precursors for ALD, we developed a series of new Co precursors by systematically introducing all nitrogen coordinating ligands to the metal center to fine-tune the volatility, reactivity, and stability. A selection of amides, imides, amide-adducts, pyrroles, and amido-amines have been studied, with particular emphasis on the influence of structural and chemical ligand variations on the physiochemical properties of the organometallic complexes.[4,5,6]. After establishing reliable synthesis routes for the range of Co complexes, characterization by complementary analysis methods (EA, EI-MS, SC-XRD) confirmed the anticipated structures and purity. Finally, thermal analysis and vapor pressure estimation gave first insights on their suitability as ALD precursors.

Among the Co complexes synthesized, the one depicted in **Figure 1 a)** were found to exhibit suitable thermal properties in terms of volatility and stability rendering them favorable for application in ALD processes. Interestingly, some complexes exhibited unusual coordination motifs: [Co{(N^{t}Bu)₂SiMe₂}₂] arranges in a rare low spin Co(IV) configuration (**Figure 1b)**) and exhibited remarkable thermal stability in TGA (**Figure 1c)**). First

saturation experiments with this compound showed the formation of a stable self-limiting monolayer on an alumina-coated quartz crystal microbalance (QCM).[6] In summary, we were successful in enlarging the precursor library of Co precursors and the study showcases, how small but distinct changes in the ligand moieties lead to significant changes in the physiochemical properties of the complexes and gives valuable insight for future precursor development.

AF-MoP-14 Optimization of the Growth of Atomic Layer Deposited Ta₂O₅ Thin Films for Large Area Electronics, *Xiao Chen, K. Niang, B. Bakhit, Y. Jeon, J. Driscoll, A. Flewitt,* University of Cambridge, UK

Tantalum oxide, Ta_2O_5, has been extensively studied as a promising high-k dielectric in semiconductor devices (1), as a capacitor dielectric in memory devices (2), and as an antireflection coating in solar cells (3). Ta_2O_5 has been deposited using various technologies, including e-beam evaporation (4), sputtering (5), and atomic layer deposition (ALD) (6, 7). Among these, ALD is particularly attractive technique due to its ability to precisely control stoichiometry as a result of the self-limiting growth process. In addition, ALD tends to produce thin films with high conformality and good uniformity over a large substrate area. This work focusses on optimization of ALD Ta_2O_5 for large area electronic applications where an amorphous morphology is favored as this allows excellent device-to-device uniformity, and substrate deposition temperature is limited by unconventional substrates such as glass and plastic.

Ta_2O_5 is grown by ALD from pentakis(dimethylamino)Ta (PDMAT) and water using a Savannah system from Cambridge Nanotech/Veeco. We have investigated various ALD process parameters such as the pulse time, purge time, substrate temperatures, and various post-deposition annealing temperatures. We have also investigated the physical, electronic and optical properties of the deposited thin films using various characterization techniques.

We show that the ALD Ta_2O_5 can be produced within a large process window and with good uniformity. At 200 °C, the saturated growth rate is ~ 0.6 Å/cycle, and thickness uniformity of ~ 95% is obtained across a 4-inch diameter wafer. The as-deposited Ta_2O_5 thin films are amorphous and require a post-deposition annealing at ~ 700 °C to become polycrystalline with a textured surface. We will correlate the morphology of the as-deposited thin films with their optical and electrical properties such as dielectric constants and breakdown voltages.

AF-MoP-15 Bismuth Alkoxides for Deposition of Bismuth Chalcogenides, *Jaroslav Charvot,* University of Pardubice, Czechia*; R. Parkhomenko, M. Knez,* CIC nanoGUNE, Spain*; A. Bahrami, K. Nielsch,* IFW Dresden, Germany*; F. Bureš,* University of Pardubice, Czechia

Bismuth chalcogenides are semiconductors with attractive properties for thermoelectric applications. ALD of Bi_2S_3,[1] BiSe,[2] Bi_2Se_3,[3,4] and Bi_2Te_3[5] was reported using various precursors. $BiCl_3$ is the most accessible precursors, but its rather low vapor pressure makes it difficult to evaporate. On the other hand, $(Me_2N)_3Bi$ is very volatile but lacks thermal stability with decomposition starting around 120 °C and suffers from aging. Bismuth alkoxides were investigated previously and (tris(2,3-dimethylbutanolate)bismuth) (DMB_3Bi) was selected, as the best candidate for Bi_2O_3 deposition.[6]

This study delves further into DMB_3Bi and its analogues, aiming to identify easily accessible and suitable precursors for depositing bismuth chalcogenides by reaction with bis(trialkylsilyl)-, bis(trialkylstanyl)selenides and tellurides. Series of alcoholates is prepared by alcoholysis of (iPr₂N)₃Bi giving corresponding Bi-alkoxides in good yields. This method allows preparation in non-polar solvents like hexane, which makes the separation of products comfortable during up-scaled synthesis. The investigation is expanded further by examination of fluorinated alcoholates, where the best results are obtained with $[(CF_3)_2CHO]_3Bi$ acquired by simple synthesis starting from tris(4-methylphenyl)bismuthine.[7] Although having a relatively high molecular mass, $[(CF_3)_2CHO]_3Bi$ features high volatility with boiling point at 115 °C (0.5 torr).

Volatility and thermal stability of prepared materials are studied and discussed. Most of prepared precursors remain stable up to 180 °C and sufficient vapour pressure is achieved by heating below 90 °C (ca. 0.5 torr) giving temperature range wide enough for application in ALD. In the last stage, the most promising candidates are tested in ALD with aim to deposit Bi_2Se_3 and Bi_2Te_3.

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AF-MoP-16 From Microscopic to Macroscopic: How Morphology Impacts ALD and CVD Nucleation Kinetics, *Andreas Werbrouck, A. Shearer, S. Bent,* Stanford University

Nucleation delay is an intrinsic part of area selective deposition (ASD), (metal) atomic layer deposition (ALD) and chemical vapor deposition (CVD). While much earlier work has been done on this topic, earlier models often substantially simplify the morphology of the film and/or nuclei. Here we fill the gap of how diffusion and reactivity impact morphology and coalescence, and vice versa.

In the first part of this work we describe a kinetic Monte Carlo (KMC) code that allows us to study the time-dependent microscopic evolution of a monolayer in time. We discern three steps in developing a full model: in the first step (reaction), a flux of reactive molecules changes the coverage with substrate- and film-dependent sticking coefficients. In the second step (diffusion), the coverage of the surface stays constant, but the material is allowed to diffuse until it reaches an absorbing state. Finally, steps 1 and 2 are combined to describe a surface that undergoes both deposition and diffusion of the film. The simulations explain how surface morphology influences the reactivity, which in its turn influences the morphology. Intermediate, metastable states include migration of particles across the surface, the merging of nuclei, and typical diffusion-limited aggregation (DLA) morphologies. This depends on the flux of incoming material, sticking coefficients, binding energies and the deposition temperature.

In the second part of this work, the microscopic insights from the KMC are translated into a macroscopic system of equations that can be solved computationally. In this model, the *edge length per surface area* of the deposited material is used as a key parameter to describe the time evolution of the coverage and the thickness. Casting the system as a mathematical problem allows for faster solving, statistical noise due to the limited system size is eliminated, and a distinction between continuous (CVD) and self-limiting (ALD) growth can be made.

Our simulations and the accompanying model explain a range of experimental observations and encompass often implicit and empirical knowledge: e.g., in ASD, why overdosing often results in poor selectivity and why longer purge times can increase the selectivity; for metal ALD, why longer precursor dosing and/or pretreatment of the substrate increase nucleation and why longer purge times change the morphology; and for deposition onto 2D materials, why widely different morphologies are observed.

AF-MoP-17 Novel Imido Cyclopentadienyl-based Niobium Precursors for Atomic Layer Deposition of Nb₂O₅ Thin Films, *Dong Hun Shin, H. Oh, J. Chun,* SK trichem, Republic of Korea*; S. Lee, W. Jeon,* Kyung Hee University, Republic of Korea*; Y. Park,* SK trichem, Republic of Korea

Niobium oxide (Nb_2O_5) has a high-k dielectric behavior that has been used in various applications such as capacitors, insulators, and sensors.[1] Nb_2O_5 thin film is also a constituent for multimetal oxide systems such as dopant with a high-k material, laminate structures.

Therefore, various Nb precursor complexes have been reported; most of these compounds have solid properties. It is known that solid precursors have disadvantages in the ALD process. Although only a few selected liquid precursors are used, most Nb precursors suffer from low thermal stability issue.[2]

Herein, we developed a novel liquid imido cyclopentadienyl-based Niobium precursor with high thermal stability (DSC = 339 ℃) to solve this problem. The thermal atomic layer deposition (ALD) of the newly developed Niobium precursor has evaluated using ozone as an oxygen source. Self-limiting Growth was observed for the growth of the Nb_2O_5 films at 300 ℃ on SiO_2 substrate and a growth per cycle (GPC) up to 0.044 nm/cycle. The deposited films exhibited an ALD window of 280 – 320 ℃, confirming their process compatibility with ZrO_2 films. And thin film properties such as

crystallinity, impurity content, and film density were confirmed through XRD, XPS, and XRR analysis. We also fabricated Nb_2O_5 doped ZrO_2 capacitors using ALD and evaluate their electrical properties such as dielectric constant and leakage current.

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AF-MoP-18 Atomic Layer Deposition of In$_2$O$_3$ Thin Films Using New In Precursor, *Donghyun Kim, H. Oh,* SK Trichem, Republic of Korea; *Y. Choi, W. Jeon,* Kyung Hee University, Republic of Korea; *Y. Park,* SK Trichem, Republic of Korea

Indium oxide (In_2O_3) thin films are vital for numerous applications with their advantages such as wide band gap, high optical transparency, electronic properties and excellent chemical stability. In_2O_3 thin films frequently are used in combination with other metals. These days, although many applications require In_2O_3 films to be high-quality in terms of thermal stability and electronic properties for proper metal ratio, but it is hard to control previous indium precursors because of its basic properties (solid phase, low vapor pressure and poor thermal stability, pyrophoric issue etc.). So, it is necessary to develop the new indium precursor to solve the existing problems.[1][2]

We developed a novel liquid indium precursor with excellent volatile ($TGA_{1/2}$: 137℃), good thermal stability (DSC : 332℃) and non-pyrophoric properties. These properties should be a suitable role in large area and high volume ALD process in addition to high temperature deposition.

The thermal atomic layer deposition (ALD) of the new indium precursor has evaluated using O_3 as an oxygen source. Self-limiting growth was observed for the growth of the In_2O_3 films at 280℃ to 350℃ on Si substrate and a growth per cycle (GPC) up to 0.1 nm/cycle at 300℃. The deposited In_2O_3 films possess a cubic phase crystalline structure without any carbon impurity. We fabricated MIM capacitor with In_2O_3 interfacial layer inserted between ZrO_2 and TiN bottom electrode at 300℃. And we evaluated their electrical properties such as dielectric constant and leakage current in priority. Through C-V and I-V data, we confirmed that inserted In_2O_3 film is helpful for capacitor to improve dielectric constant and leakage current values compared to pristine ZrO_2.

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AF-MoP-19 Reductive Surface Chemistry with Plasma Electrons, *Pentti Niiranen, D. Lundin, H. Pedersen,* Linköping University, IFM, Sweden

Depositing elemental films of electropositive metals at low temperature requires powerful reducing agents. We have recently reported on an alternative CVD scheme using plasma electrons as the reducing agents for the deposition of metallic films.[1] The process has been demonstrated using the metallocene's of Co, Fe and Ni, and in addition shown to be inherently area selective to low-resistivity areas.[2] We call the process electron CVD (e-CVD). However, the deposition chemistry is not understood and we will here describe our efforts to understand it in detail.

Despite employing a pulsed e-CVD process, separating the ferrocene and the argon plasma in time, iron films deposited from ferrocene are contaminated by high amounts of carbon. We will describe how we from quantum chemical modeling and a combination optical emission spectroscopy and mass spectroscopy have formed a plasma chemical model for ferrocene in the e-CVD plasma. From this, we attribute the carbon contamination to redeposition of cyclopentadienyl ligands upon contact with the plasma after desorption during the plasma step.

We studied the electron temperature, electron density and plasma potential in the hollow cathode discharge in our e-CVD process by a modified Sobolewski probe.[3] From these measurements we show that the presence of ferrocene in the vacuum chamber has a significant effect on the plasma characteristics, increasing the electron temperature from below 1 eV to 1-5 eV. The electron density at the substrate was found to be in the 10^{16} m^{-3} range.

Combining our models for the plasma chemistry and plasma characteristics, with mass spectrometry and our previously developed QCM for e-CVD[4], we will propose a surface chemical model for the film deposition in pulsed e-CVD and show indications of a self-limiting surface chemistry.

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AF-MoP-20 Surface Chemistry of Atomic Layer Deposited of Gallium Nitride Films at Different Process Temperatures, *houyem hafdi, P. Mpofu, H. Pedersen,* Linköping University, IFM, Sweden

Gallium nitride (GaN) is a commonly used semiconductor owing to its high chemical and thermal stability, which makes it suitable for various applications in modern electronics. The deposition of such materials is favored by atomic layer deposition (ALD) using e.g., triethylgallium (TEG) as a precursor. This study comes as a follow up to our previous work[1] where we proposed a surface ligand removal in ALD of GaN with TEG and NH_3 plasma by adding an additional reactive pulse between the TEG and NH_3/Ar plasma. We hypothesized that the release of C_2H_6 and C_2H_4 leads to the formation of a hydrogen-terminated surface.

Herein, we tested these hypotheses using mass spectrometry to assess the surface chemistry of GaN deposited using ALD with TEG and NH_3 at different substrate temperatures (200–400 °C) and by adding either an Ar plasma pulse (100 SCCM with 2000 W plasma power), H_2 gas pulse (50 SCCM H_2 mixed with 100 SCCM Ar), or H_2 plasma pulse (50 SCCM H_2 mixed with 100 SCCM Ar and 2000 W plasma power). Detailed identification of potential gases released during GaN deposition will be presented and discussed for the hypothesis of surface ligand removal by a reactive extra pulse in the ALD cycle.

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AF-MoP-21 Tuning the Wet Etch Rate of Silicon Dioxide Deposited by Plasma-Enhanced Atomic Layer Deposition, *Keerthi Dorai Swamy Reddy, M. Lisker,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany

Silicon oxide (SiO_2) is one of the quintessential materials necessary for the fabrication of semiconductor devices. Its application in the fabrication varies from being used as an etch stop layer, gate spacer, protective layer to protect sensitive areas around active devices and to maintain their feature size, capping layer, liner oxide, and insulating layer in the formation of through-silicon-via (TSV). Each application has one or many specific stringent requirements such as uniform thickness, stoichiometric layer deposition, minimal impurity content, lower surface roughness, conformality in high aspect ratio structures, low or high wet etch rates, and lower thermal budget. Commonly used deposition methods for SiO_2 are thermal oxidation, low-pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD), and atomic layer deposition (ALD). Although thermal oxidation and LPCVD deposition methods can deposit SiO_2 complying with most of the requirements, they have higher thermal budgets and poor step coverage. PECVD can reduce the thermal budget but also results in poor step coverage. Thermal ALD overcomes these disadvantages but can obtain lower wet etch rates only at deposition temperatures above 300 °C. In contrast, the plasma-enhanced atomic layer deposition (PEALD) can obtain low wet etch rates at lower deposition temperatures. Applications like etch stop layer and liner oxide require low wet etch rates similar to thermally grown SiO_2 while applications like insulating layer for TSV formation do not require low wet etch rates. In our work, we study how process parameters in PEALD can be varied so that a spectrum of different wet etch rates can be obtained from a single deposition method and utilized for various applications.

In this work, PEALD of SiO_2 is deposited in a direct plasma ALD tool using Bis(diethylamino)silane and Oxygen as precursors with Argon as the carrier gas at 250 °C. The dependence of process parameters such as RF power and plasma exposure duration has been studied to understand its effect on wet etch rate in Hydrofluoric acid. Figure 1 (PDF) shows the dependence of the etch rate (nm/min) on RF power and plasma exposure time. For a lower RF power (50 W), SiO_2 with a wet etch rate as high as 22 nm/min is deposited which can be applied for TSV formation whereas when RF power is

increased to 150 W, SiO$_2$ with a low wet etch rate of 7.5 nm/min is obtained which can be applied for gate spacer, liner oxide, and similar applications. The quality of the deposited layers is investigated further by employing various metrology techniques.

AF-MoP-23 ALD of Nd$_2$O$_3$ and ALD/MLD of Nd-Organic Thin Films Using New Precursor Combinations, *Florian Preischel,* Ruhr University Bochum, Germany*; A. Ghazy,* Aalto University, Finland*; J. Debus,* TU Dortmund, Germany*; D. Rogalla,* Ruhr University Bochum, Germany*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

The unique 4f-electron shell configuration of rare earth (RE) materials results in exceptional magneto-optical properties. Specifically, Nd$_2$O$_3$ thin films feature efficient luminescence and its f-f transitions, that are highly sensitive to external stimuli, could be utilized for next-generation multi-parametric sensors.[1] In this perspective, hybrid Nd-organic materials are especially appealing, as appropriate organic molecules can serve as photoluminescence sensitizers and mitigate concentration quenching effects.[2] Nd$_2$O$_3$ is further known for its high dielectric constant with a low leakage current and could serve as a gate dielectric in downscaled metal oxide semiconductor field-effect transistors.[3]

Atomic layer deposition (ALD) and combined atomic/molecular layer deposition (ALD/MLD) for hybrid materials, are most favored methods for downscaling of layers due to their precise thickness control and possibility to tune the properties of the resulting material via the process conditions and precursor chemistry. Yet, the full potential of Nd$_2$O$_3$ ALD has been constrained, with [Nd(thd)$_3$] being the only precursor examined. Its oxygen-coordination results in poor reactivity, necessitating high deposition temperatures and restricting the range of possible organic co-reactants for ALD/MLD.[4,5] This state-of-the-art scenario is a unique opportunity to explore the chemistry of Nd complexes and identify other suitable candidates.

In our search for new Nd precursors, we explored the amidinate-based precursor [Nd(DPAMD)$_3$], where the chelating ligands stabilize the complex, while the M − N bonds facilitate the desired reactivity, as evidenced in our work on CVD of Nd$_2$S$_3$ and related RE materials.[6,7]

Employing [Nd(DPAMD)$_3$] with water in a thermal ALD process, we achieved the deposition of polycrystalline cubic Nd$_2$O$_3$ thin films on silicon substrates under moderate conditions (**Figure 1**). Thereby, the GPC was constant around 1.5 Å in the ALD window from 200 °C to 300 °C. Moreover, the reactivity and versatility of [Nd(DPAMD)$_3$] were demonstrated in proof-of-principle ALD/MLD experiments. Beyond the formation of hybrid layers with the frequently used terephthalic acid (TPA), initial experiments with other organics were promising, as confirmed by FT-IR (**Figure 2**). Our work thus broadens the spectrum of available organics and lays the foundation for the fabrication of previously inaccessible hybrid materials.

Ongoing studies are focused on phase control via the process parameters, investigating the properties of the Nd$_2$O$_3$ films by Raman scattering and magneto-photoluminescence spectroscopy and extending the range of organic co-reactants for ALD/MLD.

AF-MoP-24 Thermal Atomic Layer Deposition of Aluminum Nitride Films Using Tris(dimethylamido)aluminum and NH$_3$, *O. Kim, H. Han,* **Jian Heo,** *Y. Choi, C. Kim, H. Kim,* Sejong University, Republic of Korea*; H. Kim, J. Park,* Hansol Chemical Co., Ltd., Republic of Korea*; W. Lee,* Sejong University, Republic of Korea

Aluminum nitride (AlN) is a dielectric material with high thermal conductivity and electrical resistivity that is being investigated as an insulating or buffer layer for nitride semiconductor devices. However, they are typically prepared by chemical vapor deposition (CVD), which makes integration with temperature-sensitive substrates difficult. Therefore, atomic layer deposition (ALD), which can ensure low process temperature, is required for these applications. Currently, the ALD literature using suitable Al precursors is limited. AlCl$_3$ suffers from high process temperature and Cl impurities. ALD using Al(CH$_3$)$_3$ requires NH$_3$ plasma as a co-reactant and showed high impurity levels in the film at temperatures of 325°C or higher due to insufficient thermal stability. Thermal ALD using Al(N(CH$_3$)$_2$)$_3$ (TDMAA) has also been reported at 170–400°C [1, 2], but detailed growth kinetics, film properties, and step coverage have not been described. In the present study, we report the effect of process temperature on the growth and properties of AlN films produced by the thermal ALD process using TDMAA and NH$_3$. First, we investigated the growth kinetics by examining the saturation doses of TDMAA and NH$_3$ and the ALD temperature window. Then, we investigated the film properties of the deposited films, such as composition, density, crystallinity, leakage current, and step coverage, at different temperatures ranging from 200–

350°C. Finally, we discuss the effects of deposition temperature during thermal ALD of AlN.

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AF-MoP-25 High-Temperature Atomic Layer Deposition of Silicon Oxide Thin Films Using Tris(dimethylamino)silane and Ozone, *O. Kim, Y. Choi,* **Changgyu Kim,** *H. Kim, W. Lee,* Sejong University, Republic of Korea

As the number of memory stacks of three-dimensional vertical NAND devices continues to increase, the aspect ratio of the channel hole also increases proportionally. Therefore, the use of atomic layer deposition (ALD) processes to fabricate dielectric layers is inevitable. In addition, high-temperature deposition is essential to achieve excellent film properties comparable to those of conventional oxidation-based methods. However, reports on high-temperature ALD of SiO$_2$ are limited. For ALD processes using tris-DMAS, feasibility at 200–400°C and surface reaction at 550°C have been reported [1, 2], but detailed information on growth characteristics and thin film properties have not been described, especially for temperatures higher than 600°C. In this work, we report the effect of deposition temperature on the growth kinetics and film properties of SiO$_2$ deposited by alternating injections of tris-DMAS and O$_3$/O$_2$. The deposition temperature was varied from 400°C to 700°C. First, we studied the reaction mechanism using in situ quartz crystal microbalance (QCM) at 400°C and measured the saturation dose of the precursor. Next, we investigated the growth rate and step coverage as a function of deposition temperature to determine the ALD temperature window. Finally, the physical and electrical properties of SiO$_2$ prepared at different temperatures were analyzed and compared. As a result, we propose that 600°C is the optimal ALD temperature to obtain film property and step coverage simultaneously.

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AF-MoP-26 Ozone-based Atomic Layer Deposition of Titanium Dioxide (TiO$_2$) using TTIP, *Dharsana Pulikkottil Dinesh, O. Nilsen, H. Sønsteby,* University of Oslo, Norway

Atomic layer deposition (ALD) is a key method for industrial applications of functional oxide thin films in the ICT industry; especially binary oxides for high-κ dielectrics [1, 2]. This study investigates an approach for the deposition of titanium dioxide (TiO$_2$) thin films through ozone-based atomic layer deposition (ALD) utilizing titanium isopropoxide (TTIP) as the Ti precursor. We employ TTIP as the titanium precursor due to its stability and potential for enhanced film quality [3], while ozone serves as an alternative to the traditional water-based processes, which allows Ti to be used in deposition of complex oxides. This is especially important for complex oxides where a hygroscopic intermediate is present at any stage during the process.

The deposition involves alternating exposure to the substrate with sequential pulse-purge cycles of TTIP and O$_3$, leading to the formation of TiO$_2$ thin film in a self-limiting nature. The study systematically explores the influence of process parameters such as precursor exposure time, ozone dose and temperature on the film growth and properties. Characterization techniques, including XRD, spectroscopic ellipsometry, UV-VIS spectroscopy, FTIR, and XRF, are utilized to study the surface morphology, chemical and structural characterization, substrate-film interface studies and thickness uniformity.

The results reveal a systematic understanding of the ozone-based ALD process using TTIP, with optimized deposition parameters leading to uniform and crystalline TiO$_2$ thin films. The films show promise in utilizing ozone based ALD with TTIP for deposition of higher order complex oxides containing titanium such as barium titanate, which is an excellent ferroelectric and photonic material.

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Keywords: Atomic layer deposition; thin film; Ozone-based ALD; Transition metal oxides; TTIP precursor

AF-MoP-27 Design and Installation of an Advanced Reactor for in-Situ Studies of ALD and ALE by the TU/E Technical Team, *Caspar van Bommel, M. Merkx, J. Zeebregts, C. van Helvoirt, F. van Uittert, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Advancement in atomic-scale processing requires in-depth understanding into the reaction mechanisms of deposition and etching reactions, driving the need for in-situ diagnostics during the processing. In this work, a reactor designed and installed by our group's technical team for the study of surface reactions during ALD and ALE is described, with the focus on in-situ infrared spectroscopy at sub-monolayer sensitivity.

In-situ IR spectroscopy has been demonstrated to be a very powerful tool to study the mechanisms of ALD and ALE.[1,2] However, to achieve sub-monolayer sensitivity, substrate material dependent solutions are required, i.e. the use of pressed powder, attenuated total reflection (ATR) configurations for dielectrics, or grazing incident reflection adsorption IR spectroscopy (RAIRS) for metals. To accommodate a wide range of mechanistic studies we designed the reactor with the capability for in-situ transmission and reflection IR spectroscopy. A mount on the back flange of the reactor was designed such that the sample (and sample holder) can be installed vertically (for transmission) or horizontally (for reflection).

The system is a hot wall reactor that is equipped with a loadlock, has the capability to bias the substrate for ion energy control, has up to eight precursor/inhibitor bubbler capacity, and is pumped down using a turbo-molecular pump backed with a roughing pump. Inspired on particle beam study setups in the fields of surface science and plasma physics, the setup has the option to install up to four plasma, light, or particle sources at a 45 degree angle. This option allows for individual studies on the effects of radicals, ions, and photons during ALD. Alternatively, these connections can be employed for additional in-situ diagnostics, e.g., optical emission spectroscopy (OES), quadrupole mass spectroscopy (QMS). This contribution will outline the design and capabilities of this home-built reactor.

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AF-MoP-28 Novel Hybrid Ligand Liquid Ta Precursor for High Temperature (> 480 ℃) ALD Ta2O5/TaN Process, *Hyunju Jung, K. Cho, S. Baik, W. Choi, S. Kim, J. Jeong, H. kim, H. Lee, J. Kim,* EGTM R&D, Republic of Korea

Ta_2O_5 has been developed for high-k oxide of DRAM or resistive layer of RRAM, In addition, TaN has been developed for gate metal or barrier metal of Cu interconnects in semiconductor devices.[1, 5, 7] Several liquid metal organic Ta molecules have been used for precursors of ALD Ta_2O_5 and TaN process. However, carbon impurity in the film due to low ALD temperature window of the metal organic precursors are strong obstacles to deposit impurity free film.[8] Thus, low deposition temperature is a challenge for liquid metal organic precursors to deposit high quality film.[1, 2, 4, 8]

Novel liquid Ta precursor with halide and metal organic ligand was developed for high temperature ALD Ta_2O_5 and TaN process. (Table 1). ALD window of new Ta precursor was estimated by ALD Ta_2O_5 process with O_3 reactant. Growth rate per cycle (~ 0.45 Å/cy) of ALD Ta_2O_5 is constant up to 480 ℃ (Fig 2), which is highest ALD temperature window of liquid Ta precursors reported up to now.

These organic-halide Ta precursor also has self-limiting growth characteristics. Metal organic Ta precursors tend to decompose, leading to an gradual increase in growth per cycle (GPC) with feeding time. In contrast, Halide Ta precursors has self-etching characteristics, resulting in decreased GPC with feeding time.[4, 9] The development of organic-halide ligand Ta precursors overcome challenges related to GPC saturation degradation, (Fig 1) allowing for deposition of conformal films in high aspect ratio 3D structure.

This novel liquid Ta Precursor allows its application in high-temperature ALD processes. These characteristics are crucial for deposition of high-quality thin film in semiconductor devices.[2, 4, 5]

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AF-MoP-31 Lab-Scale Fixed Bed Reactor for Atomic Layer Deposition on Particulate Materials: Initial Results, *Jorge A. Velasco, M. Ossama, C. Gonsalves, S. Larkiala, S. Andsten,* Aalto University, Finland*; K. Salonen,* ELabs Oy Engineering, Finland*; J. Rask, J. Stang, V. Miikkulainen, S. Jääskeläinen, R. Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) has developed into a valuable instrument for the preparation of porous high-surface-area heterogeneous catalysts. Once on the material, the ALD material can for example act as active sites, promoters or overcoating to postpone catalyst deactivation.

Reactor configurations such as fixed bed, fluidized bed, and rotating drum can be applied to make ALD on particulate materials. Also, reactors meant for thin film processing are used for similar purposes by placing the particulate material on a tray and letting gaseous reactants flow over and diffuse into the bed.

Operating conditions of ALD reactors for particulate materials differ significantly from mainstream thin film reactors. Larger reactant doses are needed to saturate the surface of particulate materials with surface areas of 100's of m^2 per gram (compared to ~0.1 m^2 of a typical silicon wafer). Reactant amount scales directly with the surface area to be coated. In addition, with pore diameters in the order of few to tens nanometers, typical porous materials can have extremely high aspect ratios (HAR) in the order of ~10^5. Longer reactant exposures are needed to coat HAR materials to allow the ALD reactant to diffuse into the porous structure.

From the various types of reactor configurations for ALD on particulate materials, we have chosen a fixed bed reactor since it offers an appropriate contact of gas and solid, straightforward application of heating and flow, and flexibility regarding the size and shapes of the particulate material.

The design of our self-constructed ALD reactor setup allows the coating of a few grams of porous high-surface-area materials for fundamental laboratory-scale studies. Operation can be performed under vacuum or atmospheric pressure. Loading and unloading the particulate material inertly is possible. Pre-treatment of the particulate material can take place at temperatures up to 800 ℃ under controlled gas flow. ALD reactants (liquid or powders) can be loaded inertly in reactant source vessels which can be heated up to about 200 ℃ and delivered to the reactor using a carrier gas. Delivery of gaseous sources from gas cylinders is included. The setup is equipped with an afterburner and a condenser for treating the unreacted reactant. Gas analysis of the gas stream downstream or upstream the reactor is possible at atmospheric pressure via a mass spectrometer connected online.

In this work, we present initial results of using the self-constructed ALD reactor setup. The results include the response of the temperature control system during heating and cooling steps and the performance of the reactant delivery system.

AF-MoP-32 Low Energy Ion Scattering Analysis of ALD 2D Materials, *Philipp Brüner, T. Grehl,* IONTOF GmbH, Münster, Germany*; D. Shin, A. Ruiz de Clavijo, S. Lehmann,* Leibniz Institute for Solid State and Materials Research, Dresden, Germany

2D materials, such as transition metal dichalcogenides or graphene, are a widely studied class of materials with promising applications in such fields as microelectronics, energy storage, bioengineering, or thermoelectricity [1][2]. While ALD with its self-limiting properties and sub-nm precision provides an ideal method for growing 2D materials, the physical and chemical characterization of the obtained films is challenging for surface analytical methods. Especially for ultra-thin films consisting of only few atomic layers or even a sub-monolayer only, most analytical techniques suffer from their limited surface sensitivity, often including, and thus averaging over, both the deposited film and the growth substrate.

In this study, we present analytical results of low energy ion scattering (LEIS) applied to a variety of ultra-thin 2D material samples, including Sb_2Te_3 and SnSe. In LEIS, the energy spectrum of noble gas ions scattered from the sample surface is recorded. The evaluation of elemental peaks in the resulting spectra allows the quantification of the elemental composition of the first atomic layer [3]. This extreme surface sensitivity of just a single

atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of ultra-thin films. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm.

We show how combining the top atomic layer sensitivity with layer thickness information allows us to quantify the surface coverage of the deposited films, identify surface impurities with high sensitivity, and make a statement about the growth mode of the films. While ALD should in theory grow films in a perfectly controlled layer-by-layer manner, the deposited films often show various degrees of island growth, where parts of the substrate are quickly covered by a multilayer film, while other parts of the substrate have not yet begun to initiate film growth.

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AF-MoP-33 Plasma-Enhanced Atomic Layer Deposition Processes for Low-Temperature SiN$_x$ with Aminosilane Precursors, *Hyeonjin Choi, J. Kim, Y. Ko, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

In this work, a comparative study on aminosilane precursors for low-temperature plasma-enhanced atomic layer deposition (PEALD) of silicon nitride (SiN$_x$) was investigated. Dimethyl(tert-butyl)aminosilane (DMTBAS) and bis(tert-butyl)aminosilane (BTBAS) were used as silicon precursors, and ammonia (NH$_3$) was used as a nitrogen source in the PEALD processes. Process temperatures were varied from 50 to 350°C, and process conditions were optimized by precursor flow rate, ammonia flow rate, RF power, and plasma time. The effect of process variables was investigated with a spectroscopic ellipsometer(SE), X-ray photoelectron spectroscopy(XPS), and Fourier transform infrared spectroscopy(FT-IR). Growth per cycle of SiN$_x$ with DMTBAS was 1.2Å/cycle from 50 to 150°C, and BTBAS was 0.7Å/cycle from 150 to 350°C. The small molecular volume of the DMTBAS reduces the steric hindrance during initial adsorption, which enables higher growth per cycle. Additionally, the mono-ligand structure in DMTBAS results in relatively low carbon content in the SiN$_x$ films compared to those deposited with BTBAS.

AF-MoP-34 Characterization of Sticking Probability for Various ALD Chemistries Relevant for Artificial Solid Electrolyte Interphases, *Léo Lapeyre, K. Mackosz, W. Szmyt, L. Pethö, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; P. Raynaud,* LAPLACE, France*; I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

With the increasing demand for longer life time and safer batteries, atomic layer deposition (ALD) has become the method of choice for the synthesis of artificial solid electrolyte interfaces [1-3] (SEIs) due to its outstanding thickness control and conformality of deposited films, allowing the surface modification of porous cathode active material (CAM) from batteries electrodes in a unique way. In this context, the ALD process has to be optimized in order for precursors to diffuse in the high aspect ratio (AR) and porous 3D structures of CAMs, aiming for the full coverage of the active material. Namely, the diffusivity of precursors must be maximized to ensure a proper insulation of the CAM by the ALD thin films and prevent the CAM degradation induced by the electrochemical reaction with the electrolyte.

Szmyt *et al.* (2022) [4] developed a set of scaling laws describing the different ALD regimes (reaction- or diffusion-limited) and their corresponding surface coverage with respect to coating depth and sticking probability. Eq. (1) shows the expression of the coverage in the diffusion-limited regime, i.e. the dominating regime when depositing on high AR and porous substrates. From coverage profiles, this regime allows to determine the sticking probability of precursors, by measuring the coverage profile of the chemisorbed film and obtaining lambda_c. Consequently, the relation between described by Eq. (2) enables us to determine the sticking coefficient.

In our work, we apply this model to porous Si structures (series of cylindrical holes, see Fig. 1), allowing to determine the reaction front of the coating inside the pores. The penetration depth and, therefore, the sticking coefficient of given precursors can be determined, following Eq (2). By selecting specific ALD process parameters, such as the precursor pressure and the exposure time in the reactor, the penetration depth and coverage rate can be maximised. The influence of substrate temperature on the chemisorption probability is additionally investigated, in the objective of modifying the ALD regime and improve the conformality of deposited films. This optimisation step is then applied to various ALD processes involving different precursors and coating materials, including Li-based films.

AF-MoP-35 Deposition of High Quality Aluminium Fluoride Layers through Optimization of a PEALD Process using Al(CH$_3$)$_3$ and SF$_6$, *E. O'Connor, Fabian Steger, C. Sturzenegger, D. Schachtler, H. Thomé,* RhySearch, Switzerland

Metal fluorides are of interest for various applications given their properties of low refractive index, wide bandgap and high transparency. Physical vapour deposition techniques have most frequently been used to deposit Aluminium Fluoride (AlF$_3$). In recent years there have also been a few reports on the growth of AlF$_3$ via ALD. This is of increasing interest for optical applications, particularly where conformal coatings are required on component geometries of increasing complexity. In this work AlF$_3$ films were deposited using a PEALD process with a trimethylaluminum (Al(CH$_3$)$_3$) precursor and a sulfur hexafluoride (SF$_6$) plasma. The depositions were performed in an Oxford Instruments FlexAl ALD system. A number of the PEALD parameters were optimized to deposit high quality AlF$_3$ films. Spectroscopic ellipsometry results indicate that the material has a low refractive index of 1.35 (@633nm). Atomic Force Microscopy demonstrates that the layers have low surface roughness comparable to the underlying substrate. The film density of 2.95 g/cm^3 as measured through X-ray reflection compares favourably to densities previously reported for both thermal and plasma enhanced ALD of AlF$_3$. Compositional analysis to examine the incorporation of impurities shows no evidence of residual sulfur in the layers from the SF$_6$ plasma process. The optical performance of the films was also studied with regard to the PEALD process parameters, and relevant results will be presented including Laser Induced Deflection, Laser Induced Damage Threshold and Total Integrated Scattering.

AF-MoP-36 Characterization of Elemental Composition of ALD Films Using Ion Beam Analysis, *Jaakko Julin, M. Laitinen, S. Kinnunen, T. Sajavaara,* University of Jyväskylä, Finland

The knowledge of elemental composition of atomic layer deposited (ALD) films should be of interest to anyone depositing or using ALD films in some application. Ideally the stoichiometry, impurity concentrations as well as the thickness, or areal density (atoms/cm^2), of the deposited films should all be known with sufficient accuracy.

Most ALD films and interfaces contain impurities from partially reacted precursors (e.g. H, C, N, Cl, ...) or contamination from deposition tools (e.g. F) or from ambient exposure (O). Precise knowledge of the composition is often the key to understanding the electrical, optical, mechanical or other physical properties of the deposited films.

ALD films are well suited for elemental characterization with ion beam analysis (IBA) techniques using MeV ion beams. Classical IBA techniques, such as Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) require laterally homogenous films over the measured spot, typically several square millimeters. The main advantage of these methods is that they enable standard-free quantitative analysis of impurity concentrations and areal densities irrespective of the chemical composition or matrix. The depth of impurities can be determined with a depth resolution down to 1 – 2 nm at the surface. The chief disadvantage is that these methods require the use of a 1 – 3 megavolt electrostatic ion accelerator and the analysis is usually performed by a specialist in this field; typically not an ALD researcher.

This presentation aims to demonstrate the usefulness of IBA methods to the ALD/ALE community. Examples of IBA in general and RBS and ERDA in particular in ALD research will be shown. We have performed, for example, areal density measurements around 10^{14} atoms/cm^2 (1 at./nm^2) of Hf [1] and Eu [2] with relative uncertainties within few %, measured impurities in low-temperature ALD of SbO$_x$ [3], determined Fe/Zn ratios of intermetallic ALD films [4] and studied hydrogen incorporation by using heavy water as a precursor [5].

Jyväskylä actively works towards lowering the barriers of IBA, improving the commercial availability of IBA tools and analyses, reducing the footprint and complexity of the required accelerator system and developing analysis software and quality of analyses. The actions and benefits of this work are presented for the ALD community.

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AF-MoP-37 Atomic Layer Deposition of Ga_2O_3 from GaI_3 and O_3: Effect of Substrates on the Film Growth and Structure, *Aivar Tarre, L. Aarik, H. Mändar, J. Aarik,* Institute of Physics, University of Tartu, Estonia

Gallium oxide (Ga_2O_3) has a marked application potential in high-voltage power electronic devices, solar-blind radiation detectors, ferroelectric and resistive switching memory devices and functional coatings. Hence, development of novel methods for deposition of Ga_2O_3 thin films is of significant interest.

In this work, Ga_2O_3 thin films were grown by atomic layer deposition (ALD) from GaI_3 and O_3 as precursors [1]. The films were grown on single crystalline Si and $\alpha-Al_2O_3$ substrates at temperatures (T_G) ranging from 200–650 °C applying 500–1100 ALD cycles, respectively. The Ga, O and I content in the films as well as a relative growth rate were determined by X-ray fluorescence (XRF). Crystal structure of the films and their thickness, density and roughness were characterized by X-ray diffraction (XRD) and X-ray reflection (XRR) methods.

The films deposited at lower temperatures were X-ray amorphous on all substrates while those grown at $T_G\geq350$ °C on $\alpha-Al_2O_3$ (001) and at $T_G\geq450$ °C on Si were crystalline consisting of ε- or κ-Ga_2O_3 phase. The α-Ga_2O_3 phase was obtained at higher temperatures on $\alpha-Al_2O_3$ (012) but starting from as low as 275 °C when $\alpha-Cr_2O_3$ seed layers were used on Si substrates.

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AF-MoP-39 On the Trail Ancient Worlds: Comparative Study of Commercial Scandium and Yttrium Precursors, Asgard, Midgard, Vanaheim and Olympus, *Martin Wilken,* Ruhr Universität Bochum, Germany; *T. Hepp, O. Briel,* Dockweiler Chemicals GmbH, Germany; *A. Muriqi,* Tyndall National Institute, University College Cork, Ireland; *C. Cho,* Ruhr Universität Bochum, Germany; *M. Nolan,* Tyndall National Institute, University College Cork, Ireland; *A. Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Scandium and Yttrium based materials such as their oxides (M_2O_3 M=Sc;Y) have garnered significant attention in recent years due to their unique properties and versatile applications. The unique combination of high melting point, wide bandgap, high refractive index, and excellent dielectric properties makes these oxides attractive candidates for advanced electronic and optoelectronic devices, such as memory devices, and photodetectors.[1] In particular, the ability of these group 3 oxides to serve as a high-k dielectric material in thin film transistors (TFT's)[2], highlights the need for versatile low temperature atomic layer deposition (ALD) processes. There are very few Sc and Y precursors suitable for ALD, which include the homoleptic cyclopentadienyl based compounds ([MCp_3])[3], substituted tris – R-cyclopentadienyl based compounds ([$M(RCp)_3$](R=Me,Et,^iPr))[4] and the beta-diketonates ([$M(thd)_3$])[5]. These compounds are associated with certain drawbacks such as low vapor pressure, short shelf life, limited thermal stability and low reactivity.

The search for suitable precursors and former studies[6] on our highly promising structurally similar mixed ethylcyclopentadienyl, bdma and dbt (bdma=N,N'-bisdimethylaminoacetamidinato; dbt=1,3-bis(1,1-dimethylethyl)-1-triazenato) complexes ASGARD ([[($EtCp_2Sc$(dbt)]), MIDGARD ([[$EtCp_2Sc$(bdma)]), VANAHEIM ([[($EtCpSc$(dbt)_2$]) and OLYMPUS ([[$EtCp_2Y$(dbt)]]) motivated us to perform a comprehensive comparative study on these precursors. Following up on a thorough investigation on the spectroscopical, structural and thermal properties, we adopted a computational approach to evaluate their use in ALD applications (Figure 1). Structure and ligand dissociation energies were calculated and gave a first indication for its suitability as ALD precursor. Furthermore, the interaction towards oxygen and water was investigated, showing their degree of reactivity. The comparison of the most promising candidates in proof-of-concept ALD experiments have given useful insights on their suitability as precursors.

AF-MoP-40 Design and Study of N-heterocyclic Carbenes as ALD Precursors, *Mark Aloisio, E. Desroche, F. Tumino, C. Crudden,* Queen's University, Canada

Several key characteristics must be considered when developing an atomic layer deposition (ALD) precursor. Among these considerations are the ability for the precursor to form a controlled and uniform monolayer. As well, afford benign byproducts of deposition to be considered for use at processing scales. *N*-heterocyclic carbenes (NHC) are an emerging molecular thin film due to the desired precursor characteristics. These ligand-based films show superior stability in chemical extremes and resistance to thermal treatments. The use of the ligands in organometallic chemistry lies with the tunability of the NHCs through synthetic preparations. Applying this molecular knowledge, a designer ligand can be developed for a specific ALD application. This study will explain the synthetic control of the NHCs and show film characterization via scanning tunneling microscopy to view film density on a crystalline metallic surface.

AF-MoP-41 ALD at 50: Collaborations, Topic Modeling, and Intersection with Atomic Layer Etching and Area Selective Deposition, *E. Alvaro,* Northwestern University; *Angel Yanguas-Gil,* Argonne National Laboratory

Over the past 50 years atomic layer deposition has experienced tremendous growth in terms of publications, authors, and topics. In a prior work, we conducted a longitudinal study exploring the evolution of ALD as a field as seen through the lens of scientific literature.[1] Using bibliometric and network analysis, we were able to observe the evolution of the field from three independent collaboration networks to one giant collaboration network spanning all countries and topics, a reflection of the maturity and increasing integration of the ALD community as a research field.

In this work, we extend this study to the present day and explore the interaction of the ALD community with two adjacent fields: atomic layer etching and area selective deposition. Leveraging more powerful analysis tools, we apply machine learning methods to understanding the different themes cutting across the ALD literature. Finally, we apply a similar methodology to the fields of atomic layer etching and area selective deposition and explore the overlap with ALD.

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AF-MoP-42 MoO_2 DRAM Bottom Electrode by Thermal ALD Using a New Liquid Mo Precursor, *Myeongho Kim, Y. Yi, I. Lee, J. Kim, H. Ryu, W. Koh,* UP Chemical Co., Ltd., Republic of Korea; *C. Hwang, W. Jeon,* Kyung Hee University, Republic of Korea

Conducting MoO_2 was proposed as an oxide electrode for DRAM. Crystal structure of monoclinic MoO_2 matches well with rutile TiO_2. ALD of high-k rutile TiO_2 film was demonstrated on MoO_2 film formed by pulsed laser deposition [1]. In this study, MoO_2 films were formed by thermal ALD on TiN using a new liquid Mo precursor with O_3, followed by post-deposition annealing (PDA). A metal-insulator-metal (MIM) capacitor structure was created using RuO_2 top electrode, ALD TiO_2 dielectric, and ALD MoO_2 bottom electrode on TiN. The dielectric constant (k) was measured as high as 100, indicating formation of high-k rutile TiO_2. XRD patterns show that monoclinic MoO_2 phase and rutile TiO_2 phase are prominent in annealed films compared to an as-deposited film (Figure 2). XPS was used to investigate relative amount of molybdenum oxidation state (+4, +5 and +6).

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AF-MoP-43 The Role of Substrate Temperature on the Self-limiting Growth of Highly (200) Oriented Cubic NiO Films via Hollow-cathode Plasma-assisted Atomic Layer Deposition, *F. Bayansal, S. Allaby, H. Saleh, B. Willis, Necmi BIYIKLI,* University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. Among them, CuO, Bi_2O_3, SnO, and NiO represent the most widely studied metal oxides which exhibit native p-type properties. NiO is of particular interest mainly due to its relative stability and promising performance as hole-transport layers in emerging solar cell device structures. However, the transport properties of NiO still needs to be substantially improved for its use as reliable transistor channel layers. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in p-type NiO films, the hole mobility is far from being sufficient, typically lower than 1 cm^2/Vs.

In an attempt to enhance the hole transport properties in low-temperature as-grown NiO layers, in this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si, SiO_2/Si, and sapphire substrates using nickelocene ($NiCp_2$) and O_2 plasmas in a 4" plasma-ALD reactor with a stainless steel-based hollow-cathode plasma (HCP) source, equipped with an *in-situ* ellipsometer. Detailed saturation studies using *in-situ* ellipsometer monitoring were carried out, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms $NiCp_2$ pulse / 10 s purge / 20 s O_2-plasma at 100 W plasma exposure / 10 s purge. To check the growth linearity and obtain thicker films for materials characterization, 800 cycle

long runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties.

The resulting NiO films are characterized for their structural, chemical, optical, and electrical properties. Films grown at 200 °C exhibit higher refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on both Si and SiO_2/Si substrates exhibit polycrystalline single-phase cubic structure (c-NiO). Furthermore, NiO films deposited on sapphire substrates showed weak grazing-incidence XRD signatures along with very strong and relatively sharp (200) peaks in the $\theta - 2\theta$ scans. An interesting observation is that the lowest substrate temperature sample (100 °C) displayed the strongest (200) peak. Hall measurements of the as-grown NiO layers on glass substrates, revealed film resistivity values about 40 ohm-cm.

AF-MoP-45 Surface Morphology Analysis for WO_x Thin Film after Post-Sulfurization, C. Chang, B. Liu, H. Chen, K. Chiu, C. Su, Y. Lin, *Yang-Yu Jhang*, Y. Pu, Taiwan Instrument Research Institute, NARlabs, Taiwan

TMDs are layered materials that can exhibit semiconducting, metallic and even superconducting behavior. In the bulk formula, the semiconducting phases have an indirect band gap. Recently, these layered systems have attracted a great deal of attention mainly due to their complementary electronic properties when compared to other 2D materials. However, these bulk properties could be significantly modified when the system becomes monolayer: the indirect band gap becomes direct. Such changes in the band structure when reducing the thickness have important implications for the development of novel applications, such as high photoluminescence (PL) quantum yield.

Previous studies have demonstrated direct sulfurization of the metal precursor as an effective route to produce large-area TMDs. In this paper, we have produced WS_2 by depositing WO_x thin films directly onto sapphire followed by sulfurization process. However, ALD technique is well known for its thickness controllability, reproducibility, wafer-level thickness uniformity and high conformality. Here, we grow WO_x films by ALD method, and the synthesized WS_2 layer retains the inherent benefits of the ALD process. The overall experiments and measurement were carried out on our homemade 6" cluster systems, which include ALD, RTP, and XPS modules. The sample transfer inside are under 5×10^{-6} torr to avoid air pollution. WO_x films were deposited on sapphire at ALD moduleat ~230℃. After that, sulfurization process was progressed at RTP module, which connected the sulfurization equipment. This equipment heats TAA powder to ~130℃ and makes it produce H_2S gas. BeforeRaman data indicated the WS_2 vibration signal appearing at 354 and 418 cm^{-1} when post-sulfurization temperature achieved to 800℃. In this work, the AFM data show WS_2 flakes starting to appear at 900℃, and its size are small than 50nm^2 generally. In-plane grazing incidence diffraction (IPGID) measurements also discover crystallinein the (110) and (100) direction becoming stronger when process temperature is larger than 900℃. Finally, photoluminescence (PL) spectra reveal its stacking orientation conditions and bandgap.

AF-MoP-46 Low-Temperature Atomic Layer Deposition Process of $SnSe_2$ Thin Films, *Alejandra Ruiz-Clavijo*, Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research, Germany

$SnSe_2$ films are deposited via atomic layer deposition (ALD) using $SnCl_4$ and $Se(SnMe_2)_3$ as Sn Se reactants, respectively. The deposition temperature window is from 80 to 100 °C, observing almost no growth above 110 °C due to Se desorption from the films. The growth per cycle (GPC) is 0.11 nm/cc at 80 °C. The as deposit films are amorphous, and present a smooth surface and compact appearance. Post-annealing of the films at 250 °C for 30 min improves the crystallinity of the films, obtaining polycrystalline films with preferred crystal orientation along the 00l direction. The optical and electronic properties of the films were characterized employing a UV-VIS spectrophotometer, and high temperature hall system.

AF-MoP-47 Conformality Characterization of Al-Doped ZnO Films Grown by Atomic Layer Deposition on Lateral High-Aspect-Ratio Test Structures, *Eero Haimi*, Aalto University, Finland; A. Philip, Aalto University, India; J. Velasco, Aalto University, Bolivia (Plurinational State of); M. Karppinen, R. Puurunen, Aalto University, Finland

Zinc oxide (ZnO) is a wide band-gap semiconductor with variety of applications as thin film material. With formation of intrinsic donors, or extrinsic doping, electrical and optical material properties of ZnO can be tuned. Accordingly, aluminum doped ZnO (AZO) is a prominent transparent conductive oxide candidate. There are growing nano-application areas, where film deposition on high-aspect-ratio structures is of interest. In this work, set of AZO, ZnO and Al_2O_3 thin films were applied on PillarHall™ lateral high-aspect-ratio (LHAR) test structures using atomic layer deposition (ALD). Well established diethylzinc (DEZ) and water as well as trimethyl aluminum (TMA) and water processes were used for ZnO and Al_2O_3 depositions, respectively. AZO films were deposited by alternating DEZ/H_2O and TMA/H_2O exposures, resulting in nanolaminate structure with nominally 10 nm ZnO layers alternating with nominally 2 nm Al_2O_3 layers. All depositions were carried out at 125℃ temperature applying long pulse/purge sequences. Conformality of the deposited films were characterized using energy dispersive electron probe X-ray microanalysis (ED-EPMA). In evaluation of targeted film thickness and structure, both X-ray reflectometry (XRR) and grazing incidence X-ray diffraction (GIXRD) were used for reference films deposited on silicon. Film penetration depth into the LHAR cavity and saturation profile shape along the cavity were analyzed. The results showed differences between saturation profiles of ZnO and Al_2O_3 as expected. In the case of AZO films, the higher proportion of ZnO deposition dominated the overall saturation profile shape. However, Al/Zn composition ratio of AZO films seemed to change along the LHAR cavity. This implies possible variation in material properties of AZO films along the cavity. Based on the results, high-aspect-ratio performance of the processes is discussed.

AF-MoP-48 Advancing Plasma Processes: Insights from Retarding Field Energy Analyzers in Ald/Ale Applications, *Angus McCarter*, T. Gilmore, A. Verma, Impedans Ltd., Ireland

Atomic layer deposition and etching (ALD/ALE) are important processes for creating nano scale patterns as they can deposit or remove layers with atomic-scale precision, excellent uniformity, and atomic level surface roughness. However, as structures become more spatially demanding and device dimensions shrink, the necessity for controllable and optimized plasma processes intensifies. To meet these challenges, careful selection of process parameters such as RF source power, bias power, pulsing frequency, and duty cycles is essential. Additionally, maintaining a damage-free surface is paramount due to ion-induced damage in plasma-assisted processes. Thus, spatial and time-resolved measurements of ion energy distribution functions and ion flux become imperative, providing valuable insights into the dynamics of energetic ions on wafers to control the process and facilitating the preservation of undamaged surfaces.

Impedans offers a comprehensive range of retarding field energy analyzers (RFEAs) designed to address the need for wafer-level measurements within plasma environments [1, 2]. Positioned at the substrate, these RFEAs offer insights into surface interactions within the plasma. The *Semion*RFEAmeasures the uniformity of positive and negative ion energies and flux hitting a surface, at multiple locations inside a plasma chamber using an array of integrated sensors. The *Quantum* is an advanced RFEA, that combines energy retarding grids with an integrated quartz crystal microbalance (QCM) allowing measurements of the ion energy and flux as well as the ion-neutral ratio and deposition rate. The ion-neutral ratio serves as a critical parameter for optimizing film properties. This talk will highlight the applications of these RFEAs in various ALD/ALE processes ranging from laboratory grade experiments to industrial tools [3-7]. Topics will include measurement challenges, innovative solutions, and successful case studies, shedding light on the transformative potential of RFEA technology in advancing plasma-assisted processes.

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AF-MoP-49 Precision Interface Engineering of CuNi Alloys by Powder ALD Toward Better Thermoelectric Performance, *Amin Bahrami*, S. He, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany; C. Jung, Max-Planck-Institut für Eisenforschung GmbH, Germany; R. He, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany; Z. Ren, University of Houston; S. Zhang, Max-Planck-Institut für Eisenforschung GmbH, Germany; K. Nielsch, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany

The main bottleneck in obtaining high-performance thermoelectric (TE) materials has been identified as how to decouple the strong

interrelationship between electrical and thermal parameters. Herein, we present a precise interface modification approach based on the powder atomic layer deposition (ALD) technology to enhance the performance of CuNi alloys. ZnO and Al_2O_3 layers as well as their combinations have been deposited on the surface of powders, typically in 10–100 ALD cycles, and their effect on the TE performance of bulks has been thoroughly investigated. The enhancement of the Seebeck coefficient, caused by the energy filtering effect, compensates for the electrical conductivity deterioration due to the low electrical conductivity of oxide layers. Furthermore, the oxide layers may significantly increase the phonon scattering. Therefore, to reduce the resistivity of coating layers, a multilayer structure is deposited on the surface of powders by inserting Al_2O_3 into ZnO. The accurate microstructure characterization shows that the Al atoms diffused into ZnO and realized the doping effect after pressing. Al diffusion has the potential to increase the electrical conductivity and complexity of coating layers. Compared to pure CuNi, *zT* increased by 128% due to the decrease in resistivity and stronger phonon scattering in phase boundaries.

AF-MoP-51 New Non-pyrophoric Metalorganic Precursor for ALD of Ga_2O_3, *Marcel Schmickler, F. Preischel, A. Devi,* Ruhr University Bochum, Germany

The number of publications on Gallium oxide (Ga_2O_3) as a thin film material has risen considerably over the past five years. This can be attributed to the promising properties of this material system for various applications that include amongst others being a transparent conductive oxide (TCO) material with a wide bandgap of 4.5 – 4.9 eV.[1] Paired with the high theoretical breakdown field strength of 7-8 MV/cm, the β-Ga_2O_3 phase is suitable for high-power applications.[2] Additionally, Ga_2O_3 thin films selectively doped with specific rare-earths were demonstrated to make red, green, and blue LEDs.[3]

The thin film deposition of group III element oxides via ALD is frequently done with the respective alkyls, which in the case of gallium is trimethylgallium (TMG). Although volatile, this precursor is highly pyrophoric and requires special precautions while handling. Additionally, it lacks the necessary reactivity towards water for thermal ALD.[4]

Encouraged by the results of our previous studies regarding the development of non-pyrophoric aluminum precursors[5,6] we extended the underlying concept of introducing intramolecularly stabilizing ligands to gallium with the scope of developing non-pyrophoric Ga precursors, yet being highly volatile and reactive. The new Ga compound is a low-melting solid with the thermal properties being very promising as depicted in the vaporization behavior illustrated in Figure 1. In this presentation, the focus is on tuning the physico-chemical properties of the Ga precursor and the subsequent ALD process development of high-quality Ga_2O_3 thin-films using this non-pyrophoric precursor.

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AF-MoP-52 Novel Molybdenum Precursor for Chemical Vapor Deposition and Atomic Layer Deposition, *Yuma Dote, A. Yao, A. Kikuchi,* Central Glass Co., Ltd., Japan

The existing 3D-NAND memory uses materials such as Cu and W for word lines. However, as the memory width increases in the future, it becomes imperative to reduce the metal liner width, among other factors. Mo, with lower resistance than W in ultra-scaled dimensions [1], exceptional processability, and being a barrierless material, emerges as a suitable candidate for next-generation interconnect materials.

Common Mo precursors for CVD and ALD include MoF_6, MoO_2Cl_2, and $MoCl_5$. Unfortunately, MoF_6 and $MoCl_5$ exhibit high reactivity, leading to substrate etching and loss during deposition. MoO_2Cl_2 is also prone to oxygen contamination [2]. In this study, we address these issues by introducing a new Mo precursor, F4M.

Herein, Mo films were deposited on TiN and SiO_2 substrates using F4M, MoF_6, and MoO_2Cl_2. Various analysis methods, including SEM, XRD, and XPS, were employed to comparatively evaluate the Mo film quality. Results indicate that F4M does not show any the substrate loss due to etching during deposition (see supplemental document ; Fig. 1,2). Additionally, F4M also deposited Mo films on TiN and SiO_2 without a seed layer with a shorter incubation time than MoO_2Cl_2. The low substrate loss and short incubation time can be attributed to the low energy required for nucleation (see supplemental document ; Fig. 3). Furthermore, the electrical properties of the deposited Mo films were evaluated using four-terminal sensing. The electrical resistivity of the Mo film deposited by F4M was 6.9 $\mu\Omega$cm (electrical resistivity of bulk Mo: 5.2 $\mu\Omega$cm), lower than Mo films deposited with other precursors (see supplemental document ; Table 1) [3]. The Mo film formed using F4M exhibited low electrical resistivity due to fewer impurities and larger Mo grain growth. Therefore, we believe that F4M is the most promising precursor for forming high-quality Mo films and is suitable for both CVD and ALD.

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AF-MoP-53 Role of Indium and Tin Elements in Zinc-Based Ternary Oxide Thin Films Grown by Atomic Layer Deposition, *Dong-Hyun Lim, I. Oh, A. Choi,* Ajou University, Republic of Korea

Amorphous oxide semiconductors (AOSs) are highlighted for their potential as channel materials, attributed to high mobility and low off current [1], leading to the exploration of diverse transition metals and the proposal of various AOS materials. [2] Among these, the In-Zn-O (IZO) system, notably In-Ga-Zn-O, and the Zn-Sn-O (ZTO) system have shown superior electrical performance due to high mobility from overlapping In^{3+} and Sn^{4+} 5s orbitals. [3] However, intrinsic differences such as ionic radius, electronegativity, and metal-oxygen bond strength between In^{3+} and Sn^{4+} result in distinct properties for IZO and ZTO materials. [4] Given these differences, further research is crucial to deepen our understanding of the roles of In and Sn in AOS materials.

In this study, we investigate the effects of incorporating In and Sn into ZnO thin films via atomic layer deposition (ALD), analyzing the film properties. To examine the electrical properties in detail, bottom-gate thin film transistors (TFTs) with varying compositions of IZO and ZTO channels were fabricated to compare performance. We observe that while single ZnO films exhibit wurtzite crystallinity, incorporating In or Sn shifts the films to an amorphous state. This incorporation also leads to a negative shift in the threshold voltage (V_{th}) for TFT devices, indicating increased film conductivity with higher In or Sn content. We compare the electrical characteristics of TFT devices based on both IZO and ZTO channels, with intermediate ratios of Zn to In and Sn, respectively. As-deposited IZO TFT is too conductive, not displaying on/off characteristic; however, after annealing in air for 1 hour, it shows improved performance with a V_{th} of -7.4 V, field effect mobility (μ_{FE}) of 59 cm^2/V s, and an I_{on} of 430 μA. Conversely, ZTO TFT displays on/off characteristic even before annealing with a V_{th} of -7.4 V, μ_{FE} of 14.8 cm^2/V s, and an I_{on} of 110 μA. This suggests that incorporating In into ZnO films makes them more conductive compared to Sn.

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AF-MoP-54 Ultra-Low Electron Temperature Plasma for Damage-Free Atomic Layer Deposition of Titanium Nitride Films: Advancements in PEALD Process Applications, *MINSEOK KIM, S. Kim, C. Lim, D. Kim, C. Chung,* Hanyang University, Korea

The characteristics of Titanium Nitride (TiN) thin films have been improved by utilizing an ultra-low electron temperature (ULET, T_e< 1 eV) plasma in the plasma-enhanced atomic layer deposition (PEALD) process. The ULET plasma is produced by an inductively coupled plasma system with a DC grid system. Ultra-low electron temperature plasma can significantly reduce damage induced by the plasma. Due to its low ion energy, there is less damage from ion bombardment caused by self-bias voltage, and the absence of UV generation reduces damage from radiation. In the ULET-PEALD process, the resistivity of TiN films is reduced to 325 $\mu\Omega$cm, compared to 430 $\mu\Omega$cm in films deposited by the conventional PEALD method. Additionally, this method has reduced the surface roughness of TiN films to 0.3 nm from 0.78 nm, as measured by Atomic Force Microscopy (AFM). The deposition of TiN films at the atomic level is verified through Auger Electron Spectroscopy (AES) and X-ray diffraction (XRD) analyses. The film thickness, measured by Scanning Electron Microscopy (SEM), indicated

a growth rate of about 1.5 Å per cycle. These enhanced characteristics of the TiN films can be explained through the physical mechanisms of ULET plasma

AF-MoP-56 Ultra Thin Diffusion Barrier Development by Utilizing Advanced Deposition Materials in ALD, *Changbong Yeon, D. Cho, J. Jung,* Soulbrain, Republic of Korea*; K. Tan,* Soulbrain, Malaysia*; J. Lim, Y. Park,* Soulbrain, Republic of Korea

As integrated circuits (IC) scaling continues to progress, both the transistor size and the gap between devices decrease, leading to various issues such as increased wiring resistance, quantum tunneling, and heat generation. Specifically, in terms of interconnect metallization, this reduction in dimensions poses significant challenges including the resistivity size effect, electro migration, and insufficient conductor space [1]. Consequently, the performance of the device becomes highly dependent on the electrical resistance rather than the processing speed of the transistor. The resistance-capacitance (RC) delay of the circuit, which determines the quality of IC performance, is primarily influenced by the electrical resistivity (ρ) of the material [1]. In order to solve the RC delay issues, the adoption of new conducting materials such as Ru and Mo is attracting attention. However, it remains challenging due to the requirements for developing suitable processes and new precursors.

Another strategy to address these RC challenges is to reduce the thickness of the diffusion barrier and increase the volume of the conducting material [1]. Typically, TiN thin film is used as a barrier material for metal films. However, films with a thickness below 25 Å exhibit poor continuity and fail as diffusion barriers due to facile crystallization of TiN in a columnar structure, resulting in high surface roughness.

In this study, our objective was to increase the volume of the conducting material by reducing the critical thickness of the diffusion barrier while maintaining excellent diffusion barrier properties. To achieve this, we introduced a new deposition material known as advanced deposition material to control surface chemical reactions such as adsorption and reaction with the reactant gas [2]. Consequently, the deposition process and film properties were significantly improved. For instance, the film density increased from 4.3 g/cm^3 to 5.2 g/cm^3, eliminating nucleation delay in the ALD process. Additionally, the surface roughness was reduced from 0.33 nm to 0.15 nm. Even at an extremely thin thickness of approximately 1 nm, we observed a conformal thin film and conducted a pinhole formation test using HF dipping to confirm the diffusion barrier properties. Based on the experimental evidence, we believe that this research will contribute to the development of new strategies for next-generation interconnect process.

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AF-MoP-57 A Novel Liquid Ruthenium Precursor and Its Successful Implementation in ALD, *Niklas Huster,* Ruhr University Bochum, Germany*; I. Selvakumar,* Ruhr University Bochum, India*; F. Preischel, J. Obenlüneschloß,* Ruhr University Bochum, Germany*; M. Gock, M. Unkrig-Bau, F. Eweiner,* Heraeus Precious Metals GmbH & Co. KG, Germany*; D. Rogalla,* RUBION - Ruhr University Bochum, Germany*; A. Devi,* Ruhr University Bochum, Germany

With the semiconductor industry reaching the 2 nm node and below, Copper (Cu) as a well-established interconnect material in integrated circuits (IC's) in the back-end-of-line (BEOL) process chain is reaching its limitations due to diffusion and electromigration under operating conditions.[1] Next to Cobalt (Co), Ruthenium (Ru) is the most promising candidate to replace Cu in next generation microchips, due to higher chemical stability and shorter electron mean free path.[2] To deposit thin films homogeneously over complexly structured substrates, as in next generation 2 nm and below gate-all-around field effect transistors (GAAFETs), atomic layer deposition (ALD) is the method of choice. However, finding suitable ALD Ru-precursors matching the requirements of high vapor pressure alongside thermal stability and high reactivity is a challenging task for researchers from academia and industry likewise.

In this presentation, we report on the synthesis of a novel liquid Ru precursor and its successful utilization in a Ru ALD process. The promising thermal properties as depicted in Figure 1, prompted us to employ it for Ru metal film deposition in combination with oxygen as co-reactant. This resulted in the growth of Ru films on Si and Cu substrates in the temperature range 250 – 300 °C with a GPC of 0.8 Å. The as-deposited films were analyzed by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray reflectivity (XRR). The layer composition was determined by means of X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) which revealed the high purity of the layers. The new findings on this newly developed precursor and associated ALD process can be rated as a significant step forward to meet the demands of the semiconductor industry for the 2 nm and beyond node.

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AF-MoP-58 Tailoring the Properties of Oxide Films by Doping Using Atomic Layer Deposition Method, *Mahtab Salari Mehr, L. Aarik, T. Jõgiaas, H. Mändar,* University of Tartu, Estonia

The complex ternary compound materials have received considerable attention in the last decades due to the exhibition of superior mechanical, optical, and chemical properties compared to their binary counterparts [1,2]. The programmable cycle formula of ALD enables control of the concentration of dopant elements in the composition of the thin films. Aluminum oxide and chromium (III) oxide are well-known ceramic materials showing interesting optical, and mechanical properties (hardness, elastic modulus, wear resistance).It has been reported previously that combining Cr_2O_3 and Al_2O_3 enables to tailor the properties of these oxide films for various applications [3]. In the current research study, ternary compound Cr-Al-O thin films (thickness from 50 to 80 nm) were deposited on Si (100) substrates using the ALD deposition formula of n × (Cr(thd)$_3$-O$_3$) + m ×(TMA-O$_3$)at a deposition temperature of 275 °C. The enhancement in nanoindentation hardness values of (Cr, Al)$_2$O$_3$ films was observed compared with those of binary films. Furthermore, wear resistance measurements displayed less plastic deformation of the ternary (Cr, Al)$_2$O$_3$ films under applied wear load compared with binary Cr_2O_3 and Al_2O_3 films that exhibited ploughing-induced plastic deformation during wear. A decrease in the wear rate was observed for the ternary film with a higher hardness of 18.4 GPa and lower plasticity index value of 0.260 compared with binary oxide films (Fig. 1). Our findings showed that the deposition of multicomponent films paves the way for tailoring thin film materials with enhanced mechanical properties and wear durability for various industrial applications.

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AF-MoP-59 Low-Temperature Atomic Layer Deposition of Vanadium Oxide: Unveiling the Nucleation and Growth Mechanism, Characterization, and Its Application in Perovskite Solar Cells, *NIRANJAN SINGH BAGHEL, S. Sarkar,* Indian Institute of Technology Bombay, India

Vanadium oxide (VO-$_x$) thin films are pivotal in numerous applications ranging from smart windows to sensors, energy storage devices and solar photovoltaics. VO-$_x$ atomic layer deposition (ALD) is accomplished using sequential exposures of Vanadium (V) tri-i-propoxy oxide (VTIP) and H$_2$O for employed as a metal and oxygen sources, respectively, at low temperatures in a custom-built viscous flow reactor remains challenging, limiting their integration onto sensitive substrates. This study introduces the atomic layer deposition (ALD) technique for the growth of VO-$_x$ thin films at low temperatures, emphasising the enhancement of film uniformity, stoichiometry, and functional properties through precise process control where we explain the nucleation and growth mechanism of ALD VO-$_x$ in particular, hybrid halide perovskite surface aiming to utilize the process for photovoltaic devices in *n-i-p* configuration. We employ *in-situ* QCM to understand the deposition mechanism. Through this presentation, we reveal that not the thermodynamics but the kinetic of the deposition plays

a pivotal role for the optimal photovoltaic performance employing ALD grown VO_x as the hole transport material.

AF-MoP-60 Fermi Level Tuning of ZnO Films through Mn Doping via Atomic Layer Deposition Supercycles, *Carolina Bohórquez Martínez,* Center of Nanoscience and Nanotechnology-UNAM, Mexico; *M. Domínguez de la Vega,* Institute for Research into Electronic Microscopy and Materials-UCA, Spain

The control of the electrical and mechanical properties of ZnO films is paramount for their diverse applications in electronic and optoelectronic devices. Doping with various elements presents a versatile method to tailor these properties. In this work, we investigate the doping process of ZnO films with Mn using supercycles of atomic layer deposition (ALD), allowing for precise modulation of their electrical characteristics.

We employ scanning Kelvin probe force microscopy (KPFM) to measure the contact potential difference (V_{CPD}) directly, providing invaluable insights into the influence of the dopant on the Fermi level position within the bandgap. Our results reveal changes in the work function correlated with varying Mn dopant concentrations, offering significant insights into the doping mechanism.

Additionally, we confirm the piezoelectric nature of the material through surface potential measurements, both before and after mechanical force application with a cantilever. Subsequent evaluation of the film's polarization behavior involves comprehensive measurements, including pre-polarization assessments and post-polarization analyses up to 18 hours, demonstrating the temporal stability of the polarization. Furthermore, polarization is assessed using intermittent mode, allowing for purely electrical polarization, with data acquisition facilitated through DataCube technology. Our findings unveil a strain gradient induced by polarization, indicative of inverse flexoelectricity phenomena.

This study contributes comprehensive insights into the electrical and mechanical properties of Mn-doped ZnO films grown via ALD, providing crucial knowledge for utilizing these films in various electronic and optoelectronic applications.

AF-MoP-61 Atomic Layer Deposition of HfO₂ Thin Film Using a Novel Pyrrole Based Hf Precursor, *Hyunwoo Jeong,* C. Park, K. Park, H. Kim, K. Lee, J. Park, Hansol Chemical Co., Ltd., Republic of Korea
Group 4 metal oxide materials such as ZrO_2, TiO_2, and HfO_2 have attracted considerable attention for dielectric materials for microelectronic devices. HfO_2 films has an outstanding high-dielectric constant (κ ~ 20-25, t-HfO_2), large band gap Energy (Eg ~ 6.0 eV) and good thermal stability. For these reason, the HfO_2 thin film applicate microelectronic devices such as the dynamic random access memory (DRAM) capacitors and central processing memory (CPU) gate dielectric application.

The most representative Hf precursor, CpTDMAHf (HAC), is known to exhibit excellent film properties when reacted with O_3 at 320℃. Recently, research is being conducted to develop precursors that can replace HAC under various conditions (temperature, reactant gas). We have developed precursors that can be used in either high or low temperature deposition and recently, we have designed new precursors for the application of various reaction gases.

In this study, we propose a novel pyrrole based Hf precursor namely HEP. The physical characteristic of HEP was investigated by NMR Spectroscopy. Also, we measure the properties of the HfO2 thin film of HEP against usually used HAC by thermal atomic layer deposition (TALD). For both precursors HEP and HAC, the characteristic self-limiting ALD growth mode was confirmed. HAC reacts with O_3 at 320℃ to form HfO_2 films, while HEP reacts with H_2O to form HfO_2 films.

Composition ratio of HfO_2 films were investigated by XPS. HfO_2 films deposited with HEP showed a comparable composition ratio to HAC at a lower temperature of 280℃. Also, C impurities in deposited film of HEP were 0.34%, which is lower than that of HAC (0.59%). Surface roughness of HfO_2 films were investigated by AFM. The deposited film of HEP represented comparable roughness compared to that of HAC.

From this study, The HEP is expected to be advantageous precursor for low temperature thin film deposition technique.

AF-MoP-62 Low-Carbon Silicon Oxynitride Films with Trisilylamine, *Youngju Ko,* H. Choi, J. Kim, N. Kim, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea
Silicon oxynitride (SiON) has better barrier properties than silicon oxide (SiOx) and better transmittance properties than silicon nitride (SiNx).[1] Good SiON properties are required in various industrial fields such as semiconductors, organic light emitting diodes (OLEDs) and solar cells. One of the requirement for good SiON films is low carbon impurities.[2] However, most of conventional precursors are carbon-containing precursors such as hexa-methyldisilazane (HMDS), bis(tertiarybutylamino)-silane (BTBAS), tris(dimethyl-amino)silane (TDMAS), etc.[3] In this study, trisilylamine (TSA), a carbon free precursor, was used to deposit SiON by both plasma enhanced chemical vapor deposition (PECVD) and plasma enhanced atomic layer deposition (PEALD) with minimal carbon impurities. SiON with TSA had less than 3% carbon. Compared to the conventional precursors (BTBAS, TDMAS), there was a difference in carbon content of more than 10% points. The carbon bonding state in the films was identified as C-H bonding mostly, or hydrocarbon (CxHy) functional groups contained in the conventional precursors. As the carbon content increased, the silicon and nitrogen contents decreased and Si-N bonds decreased. This study suggests that TSA, a carbon free precursor, may be a suitable precursor for the deposition of SiON films having improved film density.

AF-MoP-64 High-Temperature Atomic Layer Deposition of SiO₂ Using Metalorganic Si Precursor, *Sojeong Eom,* S. Lee, H. Yoon, S. Park, S. Na, J. Yoo, S. Jung, H. Kim, Yonsei University, Korea
Silicon dioxide (SiO_2) has been widely used in the semiconductor industry due to its good insulation properties such as wide bandgap, low leakage current, and good thermal stability. For example, high-quality SiO_2 films have been examined for use as tunneling oxide in NAND flash memory. The degradation of the device performance in 2D planar NAND was unavoidable as its integration density was increased solely through device scaling down. In this regard, vertically stacked NAND (3D V-NAND) was introduced, which could achieve a higher integration density by increasing the number of stacked layers. As a result, the device structure becomes more complex with high aspect ratio trenches. For these reasons, atomic layer deposition (ALD) is conducted for the deposition of the SiO_2 tunneling layer in 3D V-NAND. Furthermore, it requires thermal ALD rather than plasma-enhanced ALD because it usually suffers from non-conformal deposition in a high aspect ratio structure. Consequently, there has been attracted attention to the development of high-temperature thermal ALD to achieve a conformal deposition of high-quality SiO_2. For ALD SiO_2, aminosilane has been widely used, but thermal decomposition would occur at high temperatures (> 300 °C) due to its low thermal stability of the Si-H bond. $SiCl_4$ is known for good thermal stability, but it requires a large amount of exposure (> 10^9 L) and the growth per cycle (GPC) is low due to its low reactivity. In this manner, we explored high-temperature thermal ALD using ozone and aminosilane, where the Si-H is replaced with the Si-CH_3 ligands, known for better thermal stability. The growth characteristics were investigated at deposition temperatures from 100 °C to 700 °C. The saturated GPC was 1.5 Å/cycle at 500 and 600 °C, while CVD-like growth was observed at 700 °C, revealing the thermal decomposition of the Si precursor. We also compared the film quality of SiO_2 deposited at 500, 600, and 700 °C by electrical characterization of metal-oxide silicon capacitor.

AF-MoP-65 Tailoring Crystal and Electrical Characteristics of Indium Oxide via Oxygen Reactants and Substrate Temperature Control in Atomic Layer Deposition, *S. Ryu, T. Hong,* **Su-Hwan Choi**, Hanyang University, Korea; *K. Yeom, D. Ryu, J. Seok,* Hansol Chemical, Republic of Korea; *J. Park,* Hanyang University, Korea
In recent years, oxide semiconductors (OSs) have shown potential as an alternative to Si-based semiconductors due to certain advantageous properties such as high mobility, reduced off-current, and amenability to low-temperature fabrication. In addition, OSs have the advantage of being able to engineer the properties of materials by introducing various metal elements and controlling their composition, so multi-component materials such as InGaZnO, InSnGaO, InSnZnO, InGaO, and InZnO have been explored. In common, indium oxide (InO_x) is selected due to its favorable electron conduction attributes, so an in-depth understanding and controlling the factors affecting the properties of InO_x is a competitive technique for advanced engineering of its multi-component properties.

In our study, we developed a highly reactive liquid indium precursor named DMITN and controlled the energy of the surface reaction in the atomic layer deposition (ALD) process. We systematically observed the impact of various reactants (H_2O, O_3, or O_2 plasma) and substrate temperatures (100–250 °C) on the growth and characteristics of InO_x thin films. The **growth characteristics**(ALD window, growth per cycle, and step coverage) and **film properties**(impurities, stoichiometry, oxygen bonding state, crystallinity, film density, and electrical properties) differed based on the ALD process employed, ascribed to the distinct thermal energies and inherent reactivities of the chosen oxidants. Among the various factors, it was

confirmed that the degree of crystal alignment has a dominantly effect on the charge carrier mobility. Furthermore, we observed disparities in step coverage for a 40:1 high aspect ratio structure based on the type of reactant used. Notably, the use of H_2O and O_3 reactants showed superior step coverage (~95%) in comparison to O_2 plasma (~74%). Our findings suggest that the growth and properties of InO_x can be tailored by judiciously choosing the reactants according to the application requirements. Moreover, we suggest that highly reactive DMITN precursors have advantages for a wide range of applications because they can select various reactants.

AF-MoP-67 Understanding Selectivity Loss in Area-Selective ALD - a DFT Investigation of the SMI Layer Disintegration Mechanisms, *Philipp Wellmann, R. Tonner-Zech,* Wilhelm-Ostwald-Institut, Universität Leipzig, Germany

The large-scale applicability of ALD in next-generation semiconductor device manufacturing depends on the capability of area-selective process management. Most commonly, area-selectivity is achieved by inhibitor molecules binding to the non-growth surface, thereby shielding it from the ALD precursors. By choosing molecules of low molecular masses, the small molecule inhibitor (SMI) approach aims at high inhibitor vaporability for versatile application in high-volume manufacturing. Currently, the biggest challenge for SMI systems is the sustained selectivity over a satisfactory amount of ALD cycles. In a recent hybrid experimental and DFT study surveying various alkoxysilane inhibitors in blocking the deposition of Al_2O_3 on SiO_2, the optimization of the SMI ligands for prolonged selectivity could benefit from a microscopic understanding of the chemical processes involved. [1] Yet, the diminishing selectivity over time - the processes disintegrating the SMI blocking layer and initializing the growth nucleation of Al_2O_3 - remains obscure.

This DFT modeling study investigates the possible disintegration reactions of common Al precursors with realistic SMI blocking layer models of the trimethoxypropylsilane (TMPS) SMI on amorphous SiO_2 substrates. The SMI blocking layer is not inert but subject to several chemical modifications through the ALD experiment. By systematic variation of the blocking layer density, starting from a single TMPS on the surface up to a theoretical SMI layer density maximum, the dependence of the disintegration reactions on the SMI layer density is disclosed. Based on these findings, proposals for improved process selectivity are derived. The results are substantiated by an energy decomposition analysis.

1. Chemistry of Materials **2022** *34* (10), 4646-4659, doi: 10.1021/acs.chemmater.2c00513

AF-MoP-68 Nucleation of Copper ALD Films Studied with in Situ Synchrotron Measurements, *Aleksandra Figura-Jagoda, S. Klejna, M. Marzec,* AGH University of Krakow, Academic Centre for Materials and Nanotechnology, Poland*; E. Kokkonen,* Max IV Laboratory, Sweden*; A. Kwiatkowski,* AGH University of Krakow, Faculty of Physics and Applied Computer Science, Poland*; K. Maćkosz, C. Minzoni,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Szkudlarek,* AGH University of Krakow, Academic Centre for Materials and Nanotechnology, Poland*; I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; M. Sikora,* AGH University of Krakow, Academic Centre for Materials and Nanotechnology, Poland

Although atomic layer deposition of metal oxide films is well established process, fabrication of conductive metal layers still remains a great challenge. The main issue is non-uniform island growth, which leads to non-smooth and non-compact films. Furthermore, the process is highly surface-dependent [1]. In this study we used ambient pressure X-ray photoelectron spectroscopy (AP XPS) to investigate the mechanisms governing the ALD of copper thin films, taking advantage of surface and element sensitivity of the method along with its high sensitivity to the chemical state. With a few-nanometer penetration depth makes it possible to observe the reactions that occur on the surface and to distinguish bonds between different species involved, including the organic ones. Therefore, AP XPS allows for studying the nucleation stage of the ALD process and observation of the saturation of precursors on the surface during the half-cycles [2].

The investigated process was Cu ALD from copper hexafluoroacetylacetonate, $Cu(hfac)_2$, and diethyl zinc, Et_2Zn, on two chemically different substrates: silicon dioxide and platinum. In-situ XPS cycle by cycle observations of the chemical state of the deposit and the surface showed substrate-dependent behaviour of precursors in the early nucleation stages. During the same phase of ALD process we observed higher copper signal of the platinum than on silicon dioxide. Zinc contamination was present on both surfaces after the full cycle. However, the Cu/Zn atomic ratio was significantly higher at the Pt substrate. Preliminary analysis does not seem to confirm the transmetalation reaction, proposed by [3]. Nevertheless, in-situ APXPS showed to be important method for better understanding of the mechanism of the nucleation and growth of copper.

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AF-MoP-69 In-Situ Investigation of Oxidant Influence on Materials Properties of Ultrathin Cerium Oxide Films Using Novel Ce(Dpdmg)₃ Precursor, *Rudi Tschammer, J. Kosto, C. Morales,* BTU Cottbus, Germany*; M. Schmickler,* Ruhr Universität Bochum, Germany*; K. Henkel,* BTU Cottbus, Germany*; A. Devi,* Ruhr Universität Bochum, Germany*; J. Flege,* BTU Cottbus, Germany

Atomic layer deposition (ALD) has been used extensively to grow homogeneous films with excellent coverage and atomic-scale thickness control for a variety of applications. However, remaining challenges include the investigation of novel precursor-oxidant combinations aiming for high growth rates, low-temperature deposition as well as unraveling the complex interplay between film stoichiometry and oxidant choice for reducible oxides. In this work, we present a detailed investigation of ultrathin cerium oxide films grown using the novel $Ce(dpdmg)_3$ precursor with different oxidants (H_2O, O_2, and O_3). Following a surface science-based approach, we have combined operando spectroscopic ellipsometry and in-situ X-ray photoelectron spectroscopy to allow rapid process optimization and determination of film properties such as stoichiometry, contaminations, and thickness under ultra-high vacuum conditions. This way, a distinct dependence of initial Ce^{3+} content on film thickness and choice of oxidant is revealed, paving the way for tailoring the deposit properties toward different applications, e.g., gas sensing, through optimization of deposition parameters and precursor-oxidant interplay.

AF-MoP-70 Impact of the Knudsen Number on the ALD Saturation Profile Characteristics – Extended Slope Method, *C. Gonsalves, J. Velasco, J. Yim, J. Järvilehto, V. Vuorinen, Riikka L. Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) is based on the self-terminating (i.e., saturating and irreversible) gas–solid reactions of at least two compatible compounds. Investigating the saturation profile of an ALD process inside a high aspect ratio (HAR) feature has emerged as a way to obtain information of the fundamental kinetics of the process. One-dimensional lateral HAR (LHAR) structures are especially suited for saturation profile analysis, and silicon-based microscopic LHAR structures have become available (PillarHall™, Chipmetrics). For a fingerprint saturation profile obtained under Knudsen diffusion conditions [1], a simple *slope method* relates a lumped sticking coefficient describing the kinetics of an ALD reaction (assuming single-site Langmuir adsorption) to the slope of the adsorption front inside a LHAR structure [2].

In this work, we present a systematic analysis of the ALD saturation profile characteristics at a wide range of Knudsen numbers, from free molecular flow (Kn>>1, Knudsen diffusion) via transition regime (Kn~1) to continuum (Kn<<1, molecular diffusion) [3]. The simplest reaction case is considered, namely single-site Langmuir adsorption, with no generation of byproducts, and the simulations are made with the Ylilammi model [4]. We will show for example that the Knudsen number regime affects both (i) the penetration depth of the ALD film (free molecular flow resulting in the deepest penetration) and (ii) the slope of the adsorption front of the saturation profile (continuum resulting in steepest slope). On the basis of analysis of the slope of the adsorption front, we propose an extended method, where in addition to the square root relation with sticking coefficient at Kn>>1 [2], the slope has an inverse square root relation with the Knudsen number at Kn<<1.

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Monday Evening, August 5, 2024

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AF-MoP-71 Atomic Layer Deposition of Hafnium Oxide for Ferroelectric Devices, *Stijn van der Heijden,* B. Macco, E. Kessels, Eindhoven University of Technology, The Netherlands

Ferroelectric hafnium zirconium oxide (HZO) is a promising material which can be used for next-generation applications such as FeRAM and FeFET. To achieve this ferroelectric property, a solid understanding of the growth, annealing, and quenching of this alloy is required. This work focuses on the growth of hafnium oxide by atomic layer deposition. The aim is to understand the individual process first such that it can subsequently be used in conjunction with a ZrO_2 process for the creation of ferroelectric HZO.

The hafnium oxide films were deposited using the precursors $CpHf(NMe_2)_3$ and the co-reactant ozone. The films were deposited in an Oxford Instruments FlexAL™ ALD reactor on Si wafers with a native oxide. The process parameters were optimized, such that saturated growth was achieved (Fig. 1). Various material properties, such as thickness, density, stoichiometry, and crystal phase, are investigated for various deposition and annealing temperatures, as these parameters can play a significant role in the inducement of the ferroelectric orthorhombic crystal phase. Furthermore, the nucleation of HfO_2 on TiN is investigated, because the foreseen ferroelectric device structure utilizes HZO with TiN electrodes.

As the material is intended to be used in FeRAM devices, the conformality of the depositions is of profound importance. This conformality was investigated using lateral high-aspect ratio PillarHall™chips (Fig. 2a), and an explorative HfO_2 deposition reached an aspect ratio of 55 (Fig. 2b). To reach this aspect ratio, a $CpHf(NMe_2)_3$ dose of 10 seconds, and an ozone dose of 1 minute was used. In future depositions, the recombination probability of ozone on HfO_2 is going to be determined, such that the achieved aspect ratio for various ozone doses can be accurately estimated.

These results provide a solid stepping-stone for the formation of ferroelectric HZO which can be used in ferroelectric devices.

AF-MoP-72 Analysing Growth Behaviour of Low Temperature ALD ZnO Films on Meso-porous Si Gr Battery Anodes for Improved Performance SEI, *Boris Hudec,* Institute of Electrical Engineering, Slovak Academy of Sciences, Slovakia*; P. Sahoo, A. Güneren, M. Precnerová,* Centre for Advanced Materials Application, Slovak Academy of Sciences, Slovakia*; M. Pecz,* Institute of Electrical Engineering, Slovak Academy of Sciences, Slovakia*; K. Fröhlich,* Centre for Advanced Materials Application, Slovak Academy of Sciences, Slovakia

Application of ultra-thin ALD coatings has been shown to greatly improve the properties of various cathode and anode materials of Li-Ion batteries [1]. ALD oxides SnO2 and Fe2O3 and ZnO have also been demonstrated as working anode materials [2,3]. In our recent work [4], we have shown that the electrochemical performance of the silicon/graphite (Si/Gr) anodes can be improved by ultra-thin ALD ZnO coating grown at 100 °C. We have shown that the ZnO surface coating effectively modified the SEI layer, lowering the SEI and charge-transfer resistances and thereby facilitating Li-ion transport to the anode volume. As a consequence, the rate capability became significantly improved for the ZnO-coated Si/Gr anodes. The ZnO-protected Si/Gr electrode minimized the amount of Li2CO3 formation during cell cycling. In the study we have experimented with ALD ZnO films grown by 5-40 ALD cycles, coating Si/Gr anodes of ~20 um of thickness with estimated porosity of ~70%. Batteries prepared with the ZnO films grown by 20 ALD cycles has shown the highest improvement in the rate capability.

Tackling the ALD growth on battery electrodes, which are essentially thick substrates of meso-porous nature, is inherently challenging due to extreme values of effective surface area and equivalent aspect ratio. Rather low thermal stability of the binder in the electrode puts a constraint on the deposition temperature, which was kept at 100 °C in this study.

The major challenge of the process tuning lies in the evaluation of the penetration depth and thickness homogeneity of the films in the battery electrode. In this study we aim to correlate the ALD conditions to these properties, evaluated using a combination of non-invasive techniques. Selected experiments are evaluated using EDS scans on FIB-cut samples, and eventually correlated with the resulting electrochemical properties of fully assembled batteries.

AF-MoP-73 Rapid ALD by Forced Flow Through 3-Dimensional Macroscopic Nanoporous Solids, *Austin Cendejas,* ASEE Postdoctoral Fellow Residing at U.S. Naval Research Laboratory*; B. Greenberg, K. Anderson, B. Feygelson,* U.S. Naval Research Laboratory

Coating the internal surface of macroscopic high-aspect-ratio nanostructures via ALD opens new possibilities to tune optoelectronic, electrical, and mechanical properties of nanocomposites. The most common approach to achieving uniform infills has thus far been to employ static dosing, allowing precursors to defuse in, and byproducts out, of the tortuous porous networks.[1,2] The timescales for individual ALD cycles are thus on the order of 10s of minutes, raising potential concerns about precursor stability and more practically, throughput.[2] In this work, we develop a new approach to infilling macroscopic nanoporous solids in which pressure gradients on the order 10-100 Torr are employed to force precursor flow directly through the nanoporous network. This method was utilized to deposit ZnO films on the internal surface of ~2mm thick nanoparticle compacts comprised of 200 nm SiO_2 nanoparticles. The effect of upstream backing pressure (i.e. pressure gradient across the compact) and precursor partial pressure on required saturation pulse times will be explored. The effluent composition downstream of the nanoporous solid is continuously monitored via *in situ* quadrupole mass spectrometry, allowing precise determination of precursor breakthrough. Additionally, the ALD coating on the internal surface is evaluated by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy.

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AF-MoP-74 QCM the UiO Way, a Tutorial, *Ola Nilsen,* University of Oslo, Norway

Quartz Crystal Microbalances (QCM) do provide great insight into the growth dynamics of ALD and MLD processes, particularly when compared to their cost and ease of installation and operation. However, they can be misleading if you rely on the Sauerbrey equation alone. This talk will be a tutorial on how we perform QCM measurements at the University of Oslo (UiO), from hardware to software and dealing with effects like variations in temperature and evolution of surface roughness during growth, with examples of what to avoid and what works.

AF-MoP-75 Sticking Coefficients in Atomic Layer Deposition Processes, *Martin Knaut,* O. Bieg, T. Mikolajick, TU Dresden, Germany

The reaction probability of an Atomic Layer Deposition (ALD) process is often described as a sticking coefficient, yet this oversimplification disregards the existence of at least two distinct reactions arising from the separate half-cycles involved. This paper presents the impact of both reaction probabilities on film growth characteristics, dependent on the applied precursors and process parameters. Macroscopic and microscopic test structures with high aspect ratios served as the experimental setup to deposit and assess thickness profiles in undersaturated film growth regimes. Through this methodology, we analyzed the reaction probabilities with respect to specific process parameters and their effects on film growth, uniformity, and step coverage. In the case of Al_2O_3 ALD, our model process, significant differences in reaction probabilities were observed between the two half-cycles, illustrating variations in the required doses for achieving full surface saturation. Moreover, the utilization of uncoated, pre-treated, or pre-coated substrates facilitated the differentiation between heterogeneous and homogeneous film growth, unveiling the associated reaction probabilities and their impact on the necessary process parameters. This study aims to enhance understanding of the phenomena occurring during ALD film growth and to enable adaptations of processes and parameters accordingly.

AF-MoP-76 A Data-Driven Approach to Analyzing Chemical Reactions and Predicting Film Properties in SiOₓNᵧ ALD Processes, *Sung Kyu Jang*, H. Kim, J. Jeon, H. Kim, Korea Electronics Technology Institute, Republic of Korea; *H. Kim,* SurplusGLOBAL, Republic of Korea; *S. Kim, H. Kim, W. Lee, S. Kim,* Korea Electronics Technology Institute, Republic of Korea

Atomic Layer Deposition (ALD) is widely used in the semiconductor industry due to its ability to deposit materials uniformly on high aspect ratio structures. Accurate control and prediction of thin film properties, including thickness, composition and optical properties, significantly affects the productivity of the ALD process. In this study, we equipped an ALD reactor with a time-of-flight mass spectrometer (ToF-MS) to monitor the process chemistry during film growth and to predict film properties. We performed SiOxNy ALD processes at different temperatures using hexachlorodisilane (HCDS) precursors. We investigated the degradation and depletion of precursors and by-products during the silicon SiOxNy ALD process using in-process ToF-MS. We successfully produced SiOxNy films with a controlled composition without oxidants. It is achieved by controlling the temperature, which influences the formation of the bond. In addition, we evaluated the growth rate, composition, and optical and electrical properties of the ALD synthesised SiOxNy films, including ellipsometry, X-ray photoelectron spectroscopy, and current-electric field and capacitance-voltage analysis. The results showed that the presence of Si-N bonds compared to Si-O and O-N bonds increased with increasing deposition temperature, and the dielectric constant of the film also increased. Finally, an artificial neural network (ANN) was used to build a predictive model trained on the properties of the ALD synthesised SiOxNy films and in-process ToF-MS data. The ToF-MS data, reflecting the precursor decomposition process, played a key role in predicting the final properties of the films. The data-driven modelling methodology developed in this study has the potential to be applied to other thermal and plasma deposition systems in the future. This research is expected to help improve the productivity of industrial manufacturing processes.

AF-MoP-78 In-situ Quartz Crystal Microbalance Measurement of Adsorption Equilibrium for Trimethylaluminum, *Y. Wu, J. Yamaguchi, N. Sato, A. Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic Layer Deposition (ALD) is a precise and high-quality thin film deposition method that achieves film thickness accuracy on an atomic scale owing to its unique and specific deposition mechanism. The adsorption equilibrium constant (K) of a precursor is a crucial parameter that determines the feasibility of ALD design to achieve uniformity and conformality. Aluminum oxide (Al_2O_3) deposited via ALD using trimethylaluminum (TMA) and water has been a promising ALD method for decades. However, less information was collected to demonstrate the intrinsic understanding of its feasibility for ALD design using K. Quartz Crystal Microbalance (QCM) is a powerful method for measuring the adsorbed mass of the precursor during ALD, which can be used to evaluate the adsorption equilibrium and kinetics. In this presentation, QCM was used to measure the adsorption behavior of TMA during Al_2O_3 ALD.

A homemade hot-wall ALD including a commercial ceramic tubular furnace heater, a quartz tube chamber, and a customized gas supply system was used for TMA ALD and adsorption measurement. TMA and H_2O served as the precursor and reactant, respectively in the bubbler, and He was used as the carrier and purge gases. TMA was vaporized in a bubbler at 20°C with 1200 Pa and the precursor line was maintained at 80°C to prevent condensation and the chamber temperature ranged from 140 to 180 Celsius. An in-suit QCM is installed at the center of the chamber to measure the adsorption and deposition of TMA. The quartz crystals (Piezo Parts Co., Ltd) are all in AT-cut with accurate measurements of different temperatures.

Fig. 1 shows the QCM measurement of TMA absorbed mass with the partial pressure of TMA from 140 to 180 Celsius. The adsorbed mass was recorded for evaluating the equilibrium constant K with Langmuir isotherm by using the following equation: $\theta = (KP)/(1+KP)$.

Several partial pressures (P) of TMA have been introduced and surface adsorption was recorded at certain temperatures to construct the adsorption isotherm of TMA, which is shown in Fig. 2. By obtaining the saturated adsorbed amount at high pressure, it is plausible to extrapolate equilibrium constant K from the relationship between surface coverage (θ) and partial pressure (P), which is the inverse of the slope as equations show following: $(1/\theta) = 1 + (1/K)(1/P)$.

The obtained K has the temperature dependency as shown in Fig.3. The ΔG of adsorption was obtained as -84.5 kJ/mol, which is close to the value

reported by Quantum Computation (Density Functional Theory) calculations.

AF-MoP-79 Influence of N₂/Ar Plasma Exposure Time on the Growth Kinetics of Epitaxial Inn Studied by *in Situ* Grazing Incidence Small-Angle X-Ray Scattering, *Jeffrey Woodward,* U.S. Naval Research Laboratory; *S. Rosenberg,* Lockheed Martin Advanced Technology Center; *D. Boris, M. Johnson,* U.S. Naval Research Laboratory; *Z. Robinson,* SUNY Brockport; *S. Johnson,* Honeywell; *N. Nepal,* U.S. Naval Research Laboratory; *K. Ludwig,* Boston University; *S. Walton, C. Eddy,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) has significant potential as an enabler of new InN-based electronics due to its inherently low process temperatures, self-limited growth, scalability, and ability to achieve alloy compositions within miscibility gaps.[1] However, while multiple groups have reported the successful growth of epitaxial InN films with promising characteristics, the realization of true device-quality material is hindered by insufficient fundamental understandings of the PEALD processes, especially as pertains to the role of the plasma. Previously, it was found that the InN growth mode and coarsening behavior are strongly influenced by the concentrations of reactive and energetic plasma species.[2] These results highlight the tremendous level of control over the growth process and resultant film properties that can arise from deliberate tuning of the plasma properties, and as such, motivate further investigation into the relationships between various plasma properties and the growth kinetics.

In this work, we investigate the influence of plasma exposure time on epitaxial InN PEALD on GaN using *in situ* grazing incidence small-angle x-ray scattering (GISAXS), a technique which can provide a detailed description of the nanoscale structure of a film as it evolves in real-time. The PEALD process uses trimethylindium and N₂/Ar plasma as metal precursor and reactant, respectively, and is performed at 250 °C. Plasma exposure time is varied from slightly undersaturated to optimized and excessive conditions. The relationship between plasma exposure time and the growth kinetics is discussed.

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AF-MoP-80 Theoretical Explorations of Vapour Phase Infiltration, *Karl Rönnby,* Tyndall National Institute, University College Cork, Ireland; *M. Perego,* CNR-IMM, Unit of Agrate Brianza, Italy; *M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Vapour Phase Infiltration (VPI) is a type of atomic layer deposition (ALD) in which the precursor is allowed to enter the substrate's matrix, typically a polymer, rather than depositing on top of it. Precursor infiltration opens avenues for crafting hybrid materials or achieving nanopatterning when using a patterned block copolymer with different infiltration properties. To fully utilise this deposition technique, a deeper understanding of the interaction between the precursor and polymer becomes crucial. Thus, theoretical modelling of VPI is necessary to develop the process.

To efficiently model VPI, we have developed a modelling framework employing both non-periodic and periodic density functional theory (DFT) calculations. The non-periodic model was utilised to rapidly screen interactions between precursor and a gas-phase oligomer chain of the polymer. This approach allowed us to find how the precursor can bind with the polymer, the interaction energies and possible decomposition of precursor or polymer upon infiltration. The periodic model was constructed by taking oligomer chains of the polymer in a computation cell with periodic boundary conditions, creating an infinite polymer matrix. This allowed us to investigate how the precursor can interact with multiple chains, the swelling of the matrix and saturation behaviour with increasing amount of precursor.

The modelling results were compared to experimental VPI of trimethyl aluminium (TMA) into poly(methyl methacrylate) (PMMA) and poly(lactic acid) (PLA). We could then expand upon this work and extend the modelling possibilities to other precursors or polymers, gaining valuable information on the VPI processes.

AF-MoP-81 Synthesis and Characterization of Group III Precursors for Atomic Layer Deposition, *Dexter Dimova, S. Barry,* Carleton University, Canada

As device size in microelectronic structures decrease, atomic layer deposition (ALD) can be relied on to provide high surface uniformity at Angstrom level precision. Architectures such as gate-all-around (GAA) can benefit from this (Figure 1). The requirement for electropositive metals like

group III (scandium and yttrium) has become higher since these centres are excellent n-type dipole shifters,[1] and allow dipole tuning of the high-k/SiOx interface layer and simultaneously take advantage of the higher current carrying capacity of GAA FETs.

Generally, scandium and yttrium complexes have not been well explored in ALD: precursors with the general formulae M(thd)3, M(iPrAMD)3, and M(iPrCp)3 being the most prominent published precursors.[2-7] These three families of precursors are homoleptic and coordinatively saturated, with little opportunity to introduce other ligands to tune volatility or reactivity. This presentation will discuss Sc and Y compounds using our group's previously synthesized silicon-based ligand, geminal diaminosilane (gDAS).[8] The versatility of this ligand arises from the simple modification of the alkyl functional groups, giving an excellent opportunity to elaborate the structure, as well as to select from mono- and di-anionic ligands using this framework. The monoanionic version of gDAS will chelate metals with +3 centers to form a 6-coordinate homoleptic geometry (Figure 2). Coordination may also be lowered to optimize the effects of steric bulk and metal center surface reactivity through synthesis of 3- or 4-coordinate heteroleptic yttrium and scandium precursors, where X will initially be amide ligands and L will be a simple, neutral base (Figure 3).

The complexes will be structurally characterized by proton and carbon nuclear magnetic resonance, and single crystal XRD. Thermal characterization by thermogravimetric analysis and differential scanning calorimetry will be used to investigate decomposition, evaporation, vapor pressure, and melting point. Analysis from these techniques and early deposition data will allow for comparison to known group III ALD precursors and inspire a family of potential complexes.

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AF-MoP-82 Suppression of Ru-loss and Crystallization of SrRuO3 Films via Optimization of Initial RTA Steps, *Donghyung Lee,* Seoul National University, Republic of Korea

SrRuO3 (SRO) is an auspicious electrode material for next-generation dynamic random access memory capacitors utilizing SrTiO3 (STO) dielectric films due to their close lattice match.[1] Precious studies reported growing the SRO films by combining atomic-layer deposition (ALD) of SrO and pulsed-chemical vapor deposition (CVD) of RuO2, which generally results in amorphous as-deposited films.[ref] However, after post-deposition annealing (PDA) for crystallizing the SRO film, Ru concentration decreased due to volatile RuO4 formation, and the film morphology degraded by agglomeration. Therefore, these films could not serve as the optimum electrode layer. Recent studies investigated suppressing Ru-loss by Al-doping and optimizing the gas flow conditions during PDA after the SRO film deposition.[ref] Still, the genuine ALD process of the SRO film, i.e., both the SrO and RuO2 component layers are grown by the ALD mechanism, which may improve the film quality even after the PDA, is desired.

Therefore, this work reports the SRO films growth via the combined ALD of SrO and RuO2 layers using Sr(iPr3Cp)2 and Ru(EtCp)(η5-CH2C(Me)CHC(Me)O) as the Sr- and Ru-precursors, respectively. The SRO film deposited on the Al2O3 substrate was crystallized by rapid thermal annealing (RTA) at 650°C under different gas environments. Even with the ALD SRO films, an O2 gas environment was required for the SRO crystallization. When the RTA was conducted for 75s, a severe Ru loss (25% loss) was observed, which also degraded the film quality. However, when conducting RTA with O2 for 25s followed by N2 for 50s instead of O2 for 75s, the Ru-loss rate was reduced from ~25% to ~5%. The crystallinity and surface roughness of the two films were similar. As a result of these process modifications, the resistivity of the 17nm-thick film was decreased from ~1000 for the ALD/CVD film to 112 Ohm-cm for the ALD film, suggesting the substantially enhanced film quality.

AF-MoP-83 Doped SnO2 Thin Films Fabricated at Low Temperature by Atomic Layer Deposition with a Precise Incorporation of Niobium Atoms, *G. Diress Gesesse,* Institut Photovoltaïque d'Ile-de-France (IPVF), France; ***Damien Coutancier,*** UMR-IPVF 9006, CNRS, Institut Photovoltaïque d'Ile-de-France (IPVF), France; *M. Al Katrib, F. Donsanti,* Institut Photovoltaïque d'Ile-de-France (IPVF), France; *M. Bouttemy,* UMR 8180, CNRS, Institut Lavoisier de Versailles (ILV), France; *N. Schneider,* UMR-IPVF 9006, CNRS, Institut Photovoltaïque d'Ile-de-France (IPVF), France

Doped SnO2 thin films have emerged as a focus of interest to address the limitations of undoped SnO2 in various applications. SnO2 alone has garnered considerable interest in applications such as transparent conducting oxides (TCO), fuel cells, photocatalysis, dye-sensitized solar cells (DSSCs), and touch screens. However, the low doping level of SnO2 hampers its performance in these applications. The incorporation of Nb(+V) into SnO2 offers a solution to this challenge, enhancing carrier concentration and electrical conductivity. This is facilitated by the close ionic radii between Nb(+V) and Sn, enabling easy distribution within the SnO2 lattice[1]. While there have few been studies on the properties and applications of atomic layer deposition (ALD)-fabricated SnO2:Nb films[2,3], less attention has been paid to understanding the ALD growth process and its correlation with film properties. This work aims to bridge this gap by developing SnO2:Nb thin films via ALD, investigating the growth process, and exploring various film properties.

Tetrakis(dimethylamido)tin(IV) and Tris(diethylamido)(tert-butylimido)niobium(V) precursors were used for Sn and Nb, respectively, with H2O2 and H2O as reactants. Nb incorporation was studied using in-situ quartz crystal microbalance (QCM), manipulating the supercycle ratio for doping control. The sequence of precursor and reactant introduction was altered to explore its influence on doping efficiency.

Ellipsometry, SEM, and GI-XRD confirmed the successful synthesis of homogeneous SnO2:Nb thin films by ALD. XPS analysis demonstrated variations in Nb atom concentration, indicating the tunability of doping efficiency through adjustments in precursor and reactant sequences.

The resulting films exhibited high optical transparency (>95% transmission over a wide UV-Vis-IR range) and tuned electrical properties, with resistivity decreasing upon Nb doping and reaching as low as 2.87×10^{-2} Ω·cm with a carrier concentration of -5.23×10^{19} cm^{-3} and mobility of 4.11 cm^2/Vs.

In summary, Nb-doped SnO2 thin films synthesized at low temperatures (<100°C) via ALD demonstrated optimal Nb incorporation levels (<1 at.%) for enhanced electrical conductivity while maintaining high optical transparency. These findings pave the way for the integration of Nb-doped SnO2 thin films into temperature-sensitive, nanostructured optoelectronic devices.

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AF-MoP-84 ALD Deposited Lanthanum Doped HfO2 Thin Films on a Lateral High Aspect Ratio Structure (LHAR): Surface Characterization Using X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), *J. Emara, A. Kia,* ***Sascha Bönhardt,*** *C. Mart, K. Kühnel, N. Haufe,* Fraunhofer Institute for Photonic Microsystems Center Nanoelectronic Technologies, Germany; *R. Puurunen,* Aalto University, Finland; *M. Utriainen,* Chipmetrics Oy, Finland; *W. Weinreich,* Fraunhofer Institute for Photonic Microsystems Center Nanoelectronic Technologies, Germany

With the growing semiconductor industry and the need to miniaturize devices, the use of complex microscopic three-dimensional (3D) structures is on the rise. To develop and enhance these technologies, a comprehensive study of the materials involved is crucial. However, these 3D structures make surface characterization of deposited thin films challenging. To overcome this, two-dimensional (2D) PillarHall lateral high aspect ratio (LHAR) test structures are used in this work. These single-crystal silicon structures have lateral cavities with different lengths (1μm to 5 mm), aspect ratios (AR) of 2:1 to 10,000:1, and polysilicon pillars that hold up a membrane. This membrane can be easily peeled off with tape, exposing the area where the ALD thin films were deposited, and thereby facilitating surface analysis.

Thin film hafnium oxides (HfO2) are used in micro- and opto-electronic devices due to their high-*k*- properties. When doped with lanthanum (La), HfO2 becomes ferroelectric and can be used in technologies such as ferroelectric random-access memory (FRAM), tunnel junctions (FTJs) and

field-effect transistors (FeFETs). In this work, thin films of La doped HfO_2 were deposited on the LHAR structure using two different atomic layer deposition (ALD) processes: standard and three-step. To grow the doped films using standard ALD, the metal-organic precursors are injected into the process chamber alternately with an inert gas purging process in between. The three-step ALD process, where the precursors are subsequently introduced before the co-reactant (e.g. H_2O), has previously been proven to produce homogeneous aluminum (Al), silicon (Si) and La doped thin films with low defect densities and reduced internal bias fields. In this work we aim to advance the surface characterization of the La doped HfO_2 thin films prepared by using the two different ALD processes. To accomplish this, x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to analyze the uniformity and composition of the doped thin film. Imaging and analysis of the structured surface of the LHAR was possible for both techniques. Uniquely, XPS analysis of such small structures was possible using secondary electron imaging (SXI) and micro area analysis with a tunable x-ray beam down to ~7.5 µm. Both techniques provide a complementary and in-depth analysis of material formation, travel length, elemental distribution, and composition, and thus a comprehensive comparison between the ALD processes can be presented.

AF-MoP-85 Investigating and Overcoming the Challenges of Coating sub-Micron Dielectric Powders by Thermal and Plasma ALD, *Shagufta Batliwala, B. Peek, P. Chalker, A. Gardner, S. Gare,* University of Liverpool, UK*; J. Brindley,* Gencoa, UK*; R. Potter,* University of Liverpool, UK

Over the past decade, ALD has emerged as a powerful technique for uniformly coating high surface area powders for a broad range of applications, including catalysts, battery electrodes, feedstocks for additive manufacturing and pharmaceuticals. The current work aims to investigate the process conditions required for precisely controlled uniform ALD on sub-micron dielectric powders using a home-built fluidised bed-style powder coating adapter in an Oxford Instruments OpAL reactor. The adapter has been designed to coat small-scale powder batches (100 mg to a few grams).

Initially, a recipe for the deposition of VO_x on flat silicon samples was developed using Vanadium oxy tri-isopropoxide oxide (VTIP) and H_2O. Transferring this recipe to coat powders proved to be a significant challenge. Hence, this work offers an opportunity to share insights into problems associated with powder ALD such as powder outgassing, powder agglomeration, longer resident times, and parasitic CVD reactions. A Gencoa Optix remote plasma optical emissions spectrometer sensor was used on the reactor foreline to provide insights into the initial powder outgassing and optimal reactants dose and purge times.

A range of bulk particles was investigated as substrates. Extended outgassing was observed when the powders were heated under vacuum resulting in VO_x deposition when VTIP was dosed without any co-reactant doses. To address this, we investigated using pre-doses of Trimethylaluminium (TMA) before ALD of the target material. These doses resulted in the deposition of Al_2O_3 on the powder, which was an effective way to passivate the powder through gettering mechanisms. The outgassing was seen to be suppressed completely for non-porous substrates but persisted for the high surface area (~200 m^2/g) powders with nanopores. A non-porous SiO_2 powder with a nominal particle size of 0.5µm was chosen as the substrate to achieve controlled ALD.

To speed up the process and enhance the control, H_2O was switched with a Meaglow hollow cathode plasma system with O_2/Ar gas to generate oxidant species. There was strong evidence for a self-limiting ALD using the PEALD approach, but uneven deposition due to caking was observed in the powder bed for higher numbers of ALD cycles. It has been hypothesised that the static charge build-up during the longer runs was responsible for this caking. Introducing an H_2O dose after every 20 PEALD cycles significantly enhanced uniformity and minimised the caking.

Mixed metals oxide ALD using the approach developed is now being explored as a route to nano-engineer core-shell heterogeneous catalysts.

AF-MoP-86 Indium Precursors with Improved Thermal Stability for Atomic Layer Deposition of Indium Oxide, *Lukas Mai, P. Mehlmann,* Merck Electronics KGaA, Germany*; R. Higuchi,* Intermolecular, Inc.*; H. Heil,* Merck Electronics KGaA, Germany

Atomic Layer Deposition (ALD) is a critical process for fabricating semiconductor thin films with atomic precision. Indium gallium zinc oxide (IGZO) is particularly important for thin-film transistors (TFTs) due to its excellent electrical and optical properties. Precursor thermal compatibility is crucial for ALD, as indium, gallium, and zinc precursors must be deposited at the same deposition temperature. Weak point in terms of precursors was found to be trimethylindium (TMI). Despite its excellent volatility and good reactivity suitable for ALD, it is limited by its solid state at room temperature, pyrophoric nature, and low thermal stability, with a maximum deposition temperature of 250°C.

Addressing these limitations, new indium precursors have been developed with enhanced thermal stability and a melting point below 50°C to ensure consistent vapor pressure in ALD processes. Through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), we evaluated melting points, vapor pressures, and decomposition temperatures, identifying two promising candidates surpassing TMI in performance.

Both precursors show a high volatility suitable for ALD experiments. Moreover, they are designed to withstand ALD processes above 250°C, potentially matching the thermal properties of gallium and zinc precursors and enabling their use at the same deposition temperature. This was confirmed by initial ALD testing, indicating that these novel indium precursors exhibit improved thermal stability.

In conclusion, the introduction of new indium precursors with better thermal properties and handling ease marks a considerable advancement in ALD technology. This progress promises to refine the production of IGZO films, pushing the boundaries of TFT performance and the development of flexible and transparent electronic devices.

AF-MoP-87 DFT Study of Metal Precursor Pulse in Atomic Layer Deposition of Pt, *Sylwia Klejna,* AGH University of Krakow, Poland

Atomic layer deposition of metals relies on sequential pulses of metal precursor – metal-organic complex and co-reagent that removes the organic ligands to yield nanometre thin metallic target film. The chemisorption of the metal precursor on the substrate material is a crucial step in ALD process. It determines the efficiency of the deposition, setting the length of the incubation period and the nucleation dely. In this study, density functional theory (DFT) is utilized to investigate the metal precursor pulse in the $MeCpPtMe_3$-based Pt ALD(MeCp – methylcyclopenthadienyl ligand, $CH_3C_5H_4$; Me – methyl group, CH_3). Adsorption, decomposition and dehydrogenation pathways during metal precursor pulse are computed. Volatile by-products are identified: CH_4, C_2H_4 and MeCpH and the thermodynamics of these reactions are studied. The discussed processes are investigated on different surfaces: during nucleation on SiO_2 and during steady-state on the Pt substrate.

ALD for Manufacturing
Room Hall 3 - Session AM-MoP

ALD for Manufacturing Poster Session

AM-MoP-1 Thin-Film-Transistor Based ALD Sensors, *K. Yamano, H. Takeda, R. Miyazawa, M. Miura, B. Ahmmad,* **Fumihiko Hirose,** Graduate School of Science and Engineering, Yamagata University, Japan

In-situ monitoring of the ALD process, especially the surface reaction, is important to achieve the optimal condition in the ALD process. In our laboratory, the nanothick TiO_2 channel thin film transistor was developed for UV and gas sensing, where the adsorbed species affected the channel conductance. In the present study, the nanothick TFT was examined for monitoring the surface chemical reaction in the RT atomic layer deposition.

Fig. 1 shows the TiO_2 TFT used for the monitoring. The channel layer was an anatase TiO_2 film which was deposited on a SiO_2-stacked Si (100) substrate by atomic layer deposition followed by the post-annealing at 500 °C. The Si substrate was heavily doped with antimony to serve as the gate electrode. The SiO_2 layer as the gate capacitor was as thick as 300 nm. The Ti electrodes as drain and source were fabricated on the channel. The gate length and width were 60 and 1000 µm, respectively. The TiO_2 TFT was placed in the room-temperature atomic layer deposition (RT-ALD) chamber as shown in Fig.2. The gate voltage was 0 V while the drain voltage was 20 V during the measurement. In the RT-ALD, we used tetrakis(dimethyl)amido titanium (TDMAT) and plasma-excited humidified argon. The TDMAT pressure was 0.8 Pa and the flow rate of the plasma-excited humidified argon was 5 sccm. The temperature of the reaction chamber was set at RT (22 °C).

During the RTALD process, the drain current waveform was monitored as shown in Fig. 3. The drain current (I_d) was changed cyclically according to the ALD process. In the oxidization step by the plasma-excited humidified Ar, the drain current surged up sharply and then decreased to equilibrium. In the pumping step, the drain current continued to decrease. In the

adsorption step of TDMAT, the drain current increased slightly at first and then decreased. Although we have not fully understood the mechanism, we still consider that the surface oxidation and OH densities might affect the drain current. In the oxidization step, the surge-up might result from the initial oxidization of TDMAT, and the surface was covered with OH moieties. In the next pumping step, a certain amount of OH moieties might desorb from the surface as H_2O, leading to the decrease of I_d. In the TDMAT process, the TDMAT adsorbed on the surface to consume the OH moieties, which caused the decrease of the current. The strong modulation in the oxidizing step suggests that the change in the OH density is correlated with the drain current. We believe that the present TFT sensor can be used for the monitoring of the oxidizing species

AM-MoP-2 Accurate and Fast Wafer Level Conformality Analysis Method for ALD Films in Manufacturing, *Thomas Werner,* Chipmetrics OY, Germany; *M. Zaheer, J. Kinnunen, A. Philip,* Chipmetrics OY, Finland; *K. Kühnel, N. Haufe,* Fraunhofer IPMS, Germany

The 3D megatrend and miniaturization of devices in microelectronics has made both high-aspect ratio (HAR) features and conformal coating inevitable in today's semiconductor industry. The extensive list of semiconductor devices relying on HAR structures for their optimal application underscores the critical need for conformality assessment tools. The PillarHall® lateral high aspect ratio (LHAR) test structures stand out as unique measurement test vehicles for the conformality characterization of thin film coating processes1. They facilitate accurate and repeatable film penetration depth (PD) profile measurements aiding in the prediction and quantification of step coverage across various high aspect ratio structures. Here in the current research, we demonstrate the significant value of these LHAR test chips in assessing the wafer scale conformality. This knowledge is very crucial for tools aiming conformality on 200- or 300-mm wafers. In our approach, we placed 10 LHAR chips on a 200 mm wafer and aimed for 20 nm thick Al2O3 (TMA+H2O thermal ALD) deposition in a crossflow reactor. Our results indicate in some extent the influence of precursor inlet and outlet location in the ALD rection chamber on both film penetration depth and film thickness of the studied Al2O3. Apparently conformality variations on different wafer positions that can at least partially be related to the flow dynamics of the crossflow reactor. Furthermore, conformality can depend also on the presence of competing reaction mechanisms and kinetics in the high aspect ratio cavity and cavity opening area which can be derived from the location specific film penetration depth profiles (Fig. 1). Current research also focused on the industry compatible chip assembly on 300 mm pocket wafers. Contamination data from the 300 mm pocket wafer with chips are shown to demonstrate the compatibility of this approach for the FEOL applications. The study showed that PillarHall pocket wafers provide accurate information of the conformality as well as film growth mechanisms through the film penetration depth profiles in the different positions on the wafer and can be valuable tool in ALD process control and monitoring as well as tool qualification.

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AM-MoP-3 In-Situ Gas Monitoring of ALD Processes Using Remote Optical Emission Spectroscopy, *Erik Cox,* J. Brindley, Gencoa, UK; *D. Monoghan,* Gencoa

Effective and robust monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behaviour as well as being an important step in the eventual wide-spread industrialisation of the ALD technique.

Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is not often undertaken, especially at the production stage.

An alternative gas sensing technique that operates directly at pressures above 10e-4 mbar has been built around remote plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor's plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species. Importantly, this plasma, generated inside the sensor, has a sole function as a gas detector and does not affect the ALD process itself.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Previous work had demonstrated the usefulness of this technique, but limitations were encountered when using a DC voltage to generate the sensor's plasma as contamination and reduced sensitivity developed when used with certain precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. It will be demonstrated that the pulsed power technique is more effective than DC in preventing contamination of the sensor's electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products.

Examples of this sensing technique's practical uses for Al2O3 processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

AM-MoP-4 Batch Coating of Gas Lines by Atomic Layer Deposition, *Lassi Leppilahti,* D. Nevstrueva, Beneq, Finland

Gas lines in highly sensitive application e.g. in the process equipment in the semiconductor industry are typically made of stainless steel. They can be susceptible to corrosion from process gases such as ammonia or hydrogen fluoride. ALD coatings are excellent as protective coatings due to their high density and defect-free nature.

In this presentation an ALD solution for batch coating of gas lines is discussed. A special setup for coating gas lines was designed for the Beneq P800 system. In this setup the typical box-shaped reaction chamber was replaced with two manifolds splitting the gas feed into 30 parallel lines. These parallel lines could then accommodate series of gas lines substrates with total end to end length of 1 m.

30 pieces of straight 1 m long gas lines were coated with Al2O3 and Y2O3 to demonstrate the capability of the system. Film thickness and uniformity were monitored on silicon coupons placed inside the manifolds. Al2O3 was deposited from trimethylaluminium (TMA) and water. 52 nm film was grown with 1.04 Å/c growth per cycle and 4.7 % relative standard deviation. Y2O3 was deposited from tris(methylcyclopentadienyl)yttrium and water. 270 nm film was grown with 1.48 Å/c growth per cycle and 5.8 % relative standard deviation.

AM-MoP-5 Implementing of ALD in Post-CMOS-Compatible 200 mm Wafer Processes, *Rahel-Manuela Neubieser,* M. Michel, A. Litke, N. Boysen, Fraunhofer IMS, Germany; *A. Devi,* Ruhr Universität Bochum, Germany

The successful implementation of new ALD materials in standard 200 mm wafer fabrication processes poses challenges, particularly concerning post-processing stability of (semi-)conductive materials. This study addresses the critical issue of ensuring the stability of thin layers during post-processing steps such as patterning, chemical etching, and resist removal. Since ALD as a process is primarily predestined for thin layers consisting of a few monolayers, the influence of further process steps must be evaluated all the more critically due to the high surface to layer thickness ratio. For instance, ion beam etching processes can lead to photoresist cross-linking, requiring plasma ashing of the resist. Additionally, chemical selective etching may result in underetching of the photoresist, leading to alterations in critical dimensions as well as typical cleaning processes may attack the sensitive layers. The specific focus of this work is on the post-processing of MoS_2, a semi-conductive material, deposited by ALD at low temperatures (T = 100 °C) for gas sensing applications. To assess its stability and suitability for industrial high-volume processes, the sheet resistance of the MoS_2 layer is measured before and after typical post-processing steps. By analyzing the sheet resistance of the MoS_2 layer, valuable insights can be gained regarding its stability against further processing steps in semiconductor manufacturing. These insights are crucial for assessing the feasibility of integrating MoS_2 and similar ALD materials into industrial-scale processes.

AM-MoP-6 Optimization and Scale-Up of MgO Thin Film Production via Thermal Atomic Layer Deposition for Industrial Applications, *Muhammad Ahmad,* N. Lamminmäki, E. Manninen, P. Kaur, Picosun Oy, Finland

Magnesium oxide is a versatile material with insulating properties, high dielectric strength, a wide bandgap, high breakdown field, excellent stability, and durability. This study presents the fabrication of magnesium oxide (MgO) thin films via thermal Atomic Layer Deposition (ALD) utilizing sequential exposure of a magnesium precursor and its co-reactant, H2O for a batch of 25 wafers of 200 mm diameter. The self-limiting nature of the batch ALD mechanism was established through fine-tuning various parameters including canister and deposition temperatures, metal precursor exposure time, and oxidant pulse time. The film thickness was characterized using ellipsometry, revealing a growth rate of 0.95 Å/cycle. X-ray Reflectivity (XRR) analysis determined the density of the MgO thin film

to be 3.50 g/cm³ with a surface roughness of 1.3 nm. Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) confirmed the high purity of the magnesium oxide film, exhibiting a stoichiometry close to 1:1 with negligible nitrogen and carbon content and <1.5% hydrogen content. Therefore, the scalability of highly pure, stoichiometric and uniform magnesium oxide is emphasized, underscoring its suitability for industrial applications.

AM-MoP-7 Method to Evaluate Vapor and Droplet Content from a Direct Liquid Injection Vaporizer using Fourier Transform Infrared Spectroscopy, *David Curran,* MSP--A Division of TSI

In the realm of semiconductor technology, high-k dielectrics are a material at the forefront of technological advances.Chemical vapor deposition and atomic layer deposition processes of high-k dielectric precursors are typically delivered by means of a bubbler or a flow over vessel.These precursors often have low vapor pressure and are thermally sensitive, limiting the throughput of the vapor delivery system. Direct liquid injection (DLI) vaporizing systems allow the throughput of the vapor delivery system to be increased by generating nanometer to micron sized droplets of the precursors, improving the heat transfer to the liquid.However, incomplete vaporization of precursor droplets can lead to imperfections in the deposition.

The method developed in this presentation employs the use of Fourier Transform Infrared (FTIR) spectroscopy to conduct real-time measurements of vapor concentration and droplet content of the outlet stream of a DLI vaporizer delivery system.The spectral measurement yields a signature of the vapor + droplet phases present in the gas cell of the FTIR.The measurement yields two calculated efficiency values, concentration efficiency and evaporation efficiency, both of which require careful calibration to yield accurate results.

Concentration efficiency is an *in*-situ measurement of the vapor phase present in the gas cell of the FTIR, found by integrating over absorbance bands in the IR for each precursor.In this presentation, it is shown that tetraethyl orthosilicate (TEOS) vapor concentrations can be measured rapidly and with high linearity using partial least squares analysis.The molar vapor concentration reported by the FTIR is then compared to the molar concentration of liquid supplied to the DLI vaporizer and a concentration efficiency is calculated.

Evaporation efficiency is calculated to account for the non-volatility of many of the high-k dielectric precursors.When droplets are present in a participating media, spectral shifts can occur in the measured signal from the FTIR, due to attenuation through a spherical liquid.This calculation couples Mie theory and information about the spectral and thermophysical properties of the liquid phase of the precursor and the droplets generated by the DLI atomizer. By investigating portions of the IR spectra where wavelengths are on the same order of magnitude as droplet diameters in the participating media, the spectral shifts can be quantified, and an evaporation efficiency is calculated.Combined the efficiencies are used to evaluate the DLI vaporizers for high throughput chemical vapor and atomic layer deposition applications.

AM-MoP-9 Effect of Gas Injection Design on Conformality in High Aspect Ratio Structures in Batch ALD Reactor, *A. Smirnov, Y. Shustrov, Ivan Petras,* Semiconductor Technology Research d.o.o. Beograd, Serbia

ALD is typically characterized by two main steps with self-limiting reactions of reactants from the gas phase with the surface. Each step requires a certain time to ensure complete coverage of the surface by precursor and cleaning of the reactor volume. Thus, in order to improve ALD performance for 300 mm wafers and, especially, with the deep trench structures, it is necessary to increase efficiency of precursors delivery to the surfaces and shorten steps duration.

A comprehensive modeling may help to improve the precursors delivery to the field position, sidewalls, and bottom of the high aspect ratio trench at patterned wafer based on the analysis of the gas flow distribution in ALD reactor. Sensitivity analysis to the operating conditions allows tuning the recipe in order to achieve uniform deposition over the wafer and reduce the duration of precursor deposition and purging steps. However, such models require an accurate connection between reactor-scale and feature-scale (trench, hole, etc.) simulations.

This work is focused on the improvement of Al_2O_3 and HfO_2 batch ALD performance on the patterned wafers based on the re-design of gas injection system, steps duration, and operating conditions. Integrated modeling approach was developed to consider the self-consistent coupling of modeling tasks at different scales. The reactor-scale model of TMA and

$HfCl_4$ precursors delivery and purging steps include heat transfer and gas flow with chemical reactions. Feature-scale simulations provide the step coverage as the function of trench dimensions based on tracing of molecules within the trench with chemical reactions at the sidewalls and bottom. It is demonstrated for the blanket wafers, that gas injection system with side inlets provides more uniform distribution of the precursor between the wafers and about 30% shorter precursor step duration compared to vertical injection. The suggested ways to re-design the side inlets system demonstrate that the number of wafers in the batch can be increased up to 50 with reasonable duration of the deposition and purging steps. Increasing the trench aspect ratio from 20 up to 100 on the patterned wafers results in a good conformality over the entire wafer area achieved with the several times longer precursor pulses. Integration of the models at reactor and trench scales helps to identify the critical effects of reactor geometry and recipe in order to improve batch ALD process performance on the patterned wafers with high aspect ratio trenches.

AM-MoP-11 Visualizing Precursor Flow During ALD Processes, *James Maslar, B. Kalanyan,* National Institute of Standards and Technology (NIST)

The characteristics of precursor transport from a source vessel to a deposition surface depend on many factors such as gas manifold and chamber design as well as specific process conditions. Numerous techniques have been developed to monitor precursor concentrations in ALD processes, including optical and mass spectrometric techniques. The majority of techniques utilized with ALD processes offer high spectral information or high sampling rates but provide little spatial information. The lack of spatial resolution can be a limitation in many applications, particularly those involving flow in complex assemblies or with fast gas switching where it is difficult to predict gas flow patterns. Hence, flow visualization techniques find utility in a number of applications, such as in the evaluation of gas manifold and chamber design, the development of deposition recipes, and the identification of precursor flow excursions. In addition, spatially-resolved data can be used to validate reactor scale models, e.g., digital twins. In this work, precursor flow during ALD was visualized using optical absorption. Optical absorption is straight-forward to implement, making it a convenient technique for imaging measurements. However, maximizing the utility of the measurement sometimes requires interpreting the path length-integrated absorption data within the framework of three dimensional gas flow, which may require complementary flow simulations. $MoCl_5$ flow was imaged in a research grade ALD chamber (42 mm field of view) and a flow cell (12 mm field of view). These measurements were performed in the visible spectral region using an off-the-shelf 4096 x 3000 pixel CMOS camera operating at approximately 24 frames per second. Tetrakisdimethylamido titanium and isopropanol flow was imaged in a research grade ALD chamber. These measurements were performed in the infrared spectral region using an off-the-shelf 320 x 240 pixel microbolometer camera operating at approximately 30 frames per second. Different operational modes of the cameras will be illustrated and the sensitivity and detection limits will be discussed.

AM-MoP-12 Thermal Behaviour of Solid ALD Precursors: Comparison of Visual Imaging Tool and Thermogravimetric Analysis, *Jani Viljakka,* Volatec Oy, Finland; *T. Hatanpää,* University of Helsinki, Finland; *M. Lashdaf,* Volatec Oy, Finland; *M. Ritala,* University of Helsinki, Finland; *M. Tiitta,* Volatec Oy, Finland; *O. Nilsen,* University of Oslo, Norway

Precursors are the pinnacle of atomic layer deposition (ALD) growth. Whether being solid or liquid, they need to have sufficient volatility and be stable during storage and delivery. Such applicability are typically characterised by thermoanalytical methods, like thermogravimetry (TGA). It is a well-known and highly applicable technique but also has some its shortcomings.

In this work, we present our recent work on the characterization of solid ALD precursors using a visual imaging method named Optical Diagnosis Instrument (ODIN). It works under simulated ALD conditions of precursor delivery, and we compared it with the TGA method. Visual imaging and thermogravimetric methods give information about the behaviour of solid compounds under the vaporization conditions complementary to each other.

A range of solid compounds were chosen to represent various classes of compounds used in ALD (β-diketonate, amides, cyclopentadienyls, alkoxides, organic acids). The compounds were sublimed in vacuum for purification before the analysis. The sampling for the analysis was made in air or in glove box depending on the sensitivity of the compound. Melting points were measured with the Stuart SMP20 instrument.

Thermogravimetric analyses (TGA) were performed with Mettler Toledo TGA/DSC 3+ instrument in 10 mbar vacuum. ODIN-instrument based on the development made in University of Oslo and Baldur Coatings was applied to follow and quantify visual changes during heating in vacuum.

Both TGA and ODIN measurements gave valuable information of the suitability of the compounds for ALD. TGA provide information of the temperatures of different phenomena and the quantitative weight losses. The results of ODIN give insights of vaporization and visual understanding if other phenomena like oligomerization or decomposition occur for the compound during the heating. These methods save a lot of time in the screening phase of the compounds. They are also helpful in the evaluation of the success of the synthesis.

Nanostructure Synthesis and Fabrication
Room Hall 3 - Session NS-MoP

Nanostructures Synthesis and Fabrication Poster Session

NS-MoP-1 Interfacial Distortion of Sb_2Te_3-Sb_2Se_3 Multilayers via ALD for Enhanced Thermoelectric Properties, *Jun Yang, A. Bahrami, S. Lehmann, K. Nielsch,* Leibniz IFW-Dresden, Germany

Atomic layer deposition (ALD) is an effective technique for depositing multilayered thin films with precise control of layer thickness and functional properties. In this work, Sb_2Te_3-Sb_2Se_3 multilayers were synthesized using thermal ALD. The presence of both monolayer-by-monolayer and alloy structures when the thicknesses of Sb_2Te_3 and Sb_2Se_3 were reduced to 2 nm. And a decrease in the Sb_2Te_3 layer thickness led to the emergence of distinct peaks from the Laue rings, indicative of a highly textured film structure with optimized crystallinity. Density functional theory simulations revealed that carrier redistribution occurs at the interface to establish charge equilibrium, resulting in band bending. By carefully optimizing the layer thicknesses, we achieved a significant enhancement in the Seebeck coefficient, reaching a peak figure of merit (zT) value of 0.68 at 473 K. These investigations not only provide strong evidence for the potential of ALD manipulation to improve the electrical performance of metal chalcogenide multilayers but also offer valuable insights into achieving high performance in two-dimensional metal chalcogenide systems.

NS-MoP-2 Effect of Ga_2O_3 Doping in Atomic Layer Deposited SnO_2 Thin Films, *J. Bae, T. Lee, D. Lee, Hyeongtag Jeon,* Hanyang University, Republic of Korea

Tin dioxide (SnO_2) has suitable characteristics for application to thin film transistor and back-end-of-line (BEOL) devices with low melting point and wide bandgap (3.5~4.0eV). However, as the SnO_2 has property of high conductivity which decreases on/off current ratio, the study for lowering the off current is needed for improving electrical properties. Doping process with atomic layer deposition (ALD) is advantage of reducing off current and controlling precise thickness. Among the dopant elements used as an acceptor in the SnO_2 thin film, Gallium(Ga) has the nearly equal ion radius (0.62Å) to Sn^{4+} (0.69Å). Thus Ga ions can easily replace the position of Sn ions, lowering the crystal lattice mismatch. In addition, from doping process, since doped Ga ions trap the electrons around tin dioxide, off current can be reduced in comparison with none-doped SnO_2 thin film.

In this study, we examined the effect of Ga dopants used as the acceptor in tin oxide with various doping positions of Ga_2O_3 for improving on/off current ratio. Ga doped SnO_2(SnO_2:Ga) thin films were deposited using thermal ALD with TDMASn and TMG and ozone. In order to compare the electrical properties with various doping position, Ga doped SnO_2 thin films were deposited at different single Ga_2O_3 doping positions for use as channel layer. The positions of Ga doped layer were controlled by inserting a single Ga_2O_3 cycle into the 31th, 61th, 91th cycles out of 121 cycles(10nm thickness). Auger electron spectroscopy (AES) was used to analyze the atomic concentration of SnO_2:Ga. It was confirmed that Ga atoms were well located in the site around the doping position. The X-ray photoelectron spectroscopy (XPS) was used for confirming the chemical bonding state of SnO2:Ga thin films. The electrical properties were measured by using semiconductor parameter analyzer (B1500A). The value of on/off current

ratio is increased from 5.10 x 10^3 to 2.78 x 10^6 compared to none doped SnO_2. Through this study, we could examine the effect of the Ga doped tin dioxide thin films with various doping position from the comparison of structural, chemical, electrical properties.

NS-MoP-3 Lateral Conversion Synthesis of TMDs from Lithographically Patterned ALD Films, *Tevye Kuykendall,* Lawrence Berkeley National Laboratory; *A. Kemelbay,* Lawrence Berkeley National Laboratory, Kazakhstan; *S. Aloni,* Lawrence Berkeley National Laboratory

Recently, we developed a wafer-scalable method to synthesize lithographically patterned transition metal dichalcogenides (TMDs) using a process that we call "lateral conversion." The method begins with ALD deposited metal-oxide thin-films sandwiched between silica layers. Using photolithography, structures are patterned and etched into the film, exposing the edges of the metal-oxide film. The films are then heated in the presence of chalcogen precursor, which diffuses laterally converting the metal-oxide to TMD. We have demonstrated that TMDs can be synthesized using a variety of metal and chalcogen precursors. Alloys and heterostructures can also be formed by varying the chalcogen precursor during the conversion process. While the synthesis approach initially relied on photolithography to fabricate structures with micron-scale resolution, we have further reduced the dimensions to achieve sub-20nm features using a block copolymer lithography method that employs the self-assembly of nanoscale polymer structures. We have characterized these TMDs through a variety of techniques including optical microscopy, Raman spectroscopy and High resolution TEM.

NS-MoP-4 Low Temperature SiO_2 Deposition in a Fluidized Bed to Improve the Colloid Stability of Polymer Microspheres, *Rens Kamphorst,* Delft University of Technology, Netherlands

Fine particles dispersed in a liquid medium have extensive applications in various fields, including food [1] , drug delivery [2] and paints [3]. In our study, we investigated the wettability and agglomeration characteristics of polymer microspheres coated with low-temperature deposited SiO_2 ($SiCl_4$ and H_2O as reactants) in a fluidized bed atomic layer deposition (ALD) setup [4]. Surface characterization by Fourier Transform Infrared Spectrometry (FTIR) revealed the presence of a large-- number of deposited Si-OH groups within the first cycles, indicating a clear deviation from ideal ALD behavior. Utilizing various characterization techniques, including Environmental Scanning Electron Microscopy (ESEM) and Focused Beam Reflectance Measurement (FBRM), improvements in substrate-water affinity was assessed. Figure 1 displays a clear improvement of substrate-water affinity, even after a single deposition cycle. A drastic decrease in agglomerate size, water contact angle (WCA), and droplet absorption time of the powder was observed when coating was applied. Furthermore, we observed an increase in the amount of Si-OH present on the particle surface with increasing number of cycles, while no significant improvement in water affinity was found after the first coating cycles. Surface coverage was assessed by Low Energy Ion Spectrometry (LEIS), revealing a complete coverage after only 2 deposition cycles. Since no wettability improvements were observed after 2 cycles, we conclude that surface coverage is the primary factor in improving the colloid stability of particles by SiO_2 deposition.

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NS-MoP-7 Atomic Layer Deposition of Ruthenium Nanoparticles on Low Surface Energy Carbon Supports and Titania Nanotube Layers for Alkaline Hydrogen Evolution Reaction, *S. Mouli Thalluri, J. Rodriguez-Pereira, R. Zazpe, H. Sopha,* University of Pardubice, Czechia; *Jan Macak,* University of Pardubice, Brno University of Technology, Czechia

Noble metals, such as Pt, Ru, Pd, Ir, etc., have demonstrated superior performance for different catalytic and electrocatalytic applications.[1] Efforts to reduce or replace these noble metals have been made, due to their scarcity. Atomic Layer Deposition (ALD) is one of the best technique to facilitate lowering of loading mass on a support of interest.[2],[3] Besides, ALD is the most suitable technology for decorating high aspect ratio substrates using noble metal nanoparticles (NPs).[4] Due to surface energy variations that govern between noble metals and support surfaces, growth initiates as NPs and with further increase in ALD cycles, the agglomeration among NP dominates over the individual NP size increase, thus developing thin films of relatively greater thickness. It is also known that surface energy variations considerably increase the nucleation delay of noble

metals, especially for Ru. In this sense, our efforts focused on improving the functionality with pretreatments on carbonaceous supports that showed promise in reducing the nucleation delay of Ru deposited by ALD.

For electrocatalytic applications, it is important to choose the right substrates. Among the available substrates, carbon paper (CP) and titania nanotube (TNT) layers are the best options considering their physiochemical properties, availability, extensive literature and the low costs incurred when using them as support substrates in electrocatalysis and photocatalysis. Various surface modifications for CPs and variations in the morphological aspects of TNT layers have received great attention from applied fields due to their improved surface area, conductivity and stability.[5-9] The uniform decoration of these CPs and TNT layers by NPs or thin films of catalysts proved to be highly efficient and has no limits in applications.

This presentation will introduce and describe the synthesis of Ruthenium NPs using our ALD tool (Beneq TFS 200) on CP substrates and TNT layers with various aspect ratios. It will also includethe corresponding physicochemical and electrochemical characterization and the encouraging results obtained for alkaline hydrogen evolution reaction.

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NS-MoP-8 Iridium Nanoparticles for Alkaline Hydrogen Evolution Reaction Synthesized by Atomic Layer Deposition on Titania Nanotube Layers and Carbon Supports, *Jhonatan Rodriguez-Pereira, B. Bawab, R. Zazpe, J. Macak,* University of Pardubice, Czechia

The outstanding performance of noble metals such as Pt, Ru, Pd, Ir, etc., for different catalytic applications has been widely demonstrated.[1],[2] However, due to their scarcity, efforts have been made to reduce or substitute these noble metals. Atomic Layer Deposition (ALD) is one of the best technique to facilitate loading mass reduction on a support of interest.[3],[4] Moreover, ALD is the most suitable technology to decorate with noble metal nanoparticles, high aspect ratio and high surface area substrate architectures.[5] Surface energy variations between the noble metals and the support surfaces cause growth to initiate as nanoparticles (NPs) and as the number of ALD cycles increases, the agglomeration between NPs dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. These surface energy variations considerably increase the nucleation delay of noble metals. In this sense, our efforts focused on improving the functionality with pretreatments on carbonaceous supports that showed promise in reducing the nucleation delay of Ir deposited by ALD.

It is highly important to choose the right substrates for electrocatalytic applications. Among the available substrates, titania nanotube (TNT) layers and carbon paper (CP) are the best options considering their physiochemical properties, availability, extensive literature and the low costs incurred when using them as support substrates in electrocatalysis. Variations in the morphological aspects of TNT layers and several surface modifications for CPs have received great attention from applied fields due to their enhanced surface area, conductivity and stability.[6]–[9] The uniform decoration of these TNT layers and CPs by NPs of catalysts proved to be highly efficient and has virtually no limits in applications.[10]

The presentation will introduce and describe Iridium NPs synthesis by ALD on TNT layers and CP substrates, including the corresponding physicochemical and electrochemical characterization and the encouraging results obtained for alkaline hydrogen evolution reaction.

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NS-MoP-9 Improving Thermoelectric Performance in Bi-Te Powders through Precision Control of TiO2-induced Interface via Atomic Layer Deposition, *Su Min Eun, B. Choi,* Seoul National University of Science and Technology, Republic of Korea

The energy issue and global warming are ever increasing, making it urgent to find green energy conversion technologies. Thermoelectric devices play a crucial role in energy harvesting, as they can directly convert and recycle waste heat into electricity. Significant research is underway to enhance thermoelectric performance such as introducing nanostructures using atomic layer deposition (ALD) above the powder. ALD can control atomic-level film thickness with excellent step coverage and uniformity. ALD thin films increase the interfaces, boosting phonon scattering, and thereby reducing thermal conductivity. Additionally, they induce an energy filtering effect from materials with different band gaps, increasing the Seebeck coefficient from the potential difference. In addition, it can also inhibit grain growth during the sintering process. These approaches enable the acquisition of excellent thermoelectric properties, and characteristics of various thermoelectric and thin film materials have been widely reported. Coating TiO_2, known for its high conductivity among oxides and large bandgap, on Bi-Te alloy that demonstrates outstanding thermoelectric performance in the low-temperature range (300-500K) is expected to enhance thermoelectric efficiency. This is anticipated to reduce thermal conductivity while maintaining high electrical properties by phonon scattering and energy filtering effects, overcoming the trade-off relation between them, and thereby improving thermoelectric performance.

In this study, n-type $Bi_2Te_3Se_{0.3}$ (BTS) powders were ground by ball mill for 5hr, and 50, 100, and 200 cycles of TiO_2 layer was coated by ALD with rotary-type reactor using TTIP (Titanium isopropoxide) precursor and H_2O reactant at 200°C. Afterwards, BTS pellet was formed by spark plasma sintering at 50MPa and 673K for 5min. Morphological, structural, and chemical properties representing information such as the shape and distribution of powder or pellet, uniform growth of thin film, and crystallinity were analyzed through X-ray fluorescence, particle size analysis, high-resolution field enhanced scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Cs-corrected scanning transmission electron microscopy. Thermoelectric properties including thermal conductivity, thermal diffusivity, Seebeck coefficient, and resistance were measured through hall measurement, laser flash analysis, and ZEM-Ⅲ analysis. Comparing the calculated figure-of-merit (zT) based on measured properties, it was confirmed that interfacial modification through ALD can achieve approximately 27% improvement in thermoelectric performance.

NS-MoP-10 Selective Deposition of Pt Nanoparticles on 2D WS2 for Enhanced Photodetection, *Hwi Yoon, D. Shin, I. Sohn,* Yonsei University, Republic of Korea; *T. Nakazawa,* TANAKA Kikinzoku Kogyo K.K, Japan; *S. Chung, H. Kim,* Yonsei University, Republic of Korea

2D transition metal dichalcogenides (2D TMDCs) with thin and flexible structures have considered promising materials for nanoelectronics technology. In particular, 2D TMDCs-based photodetector is a promising candidate for a visible-light photodetector due to the high mobility and absorption coefficient of TMDC materials.However, the photoresponsivity of 2D TMDCs-based photodetectors is limited by the insufficient presence of photosensitized states caused by inherent surface defects. When exposed to light, the trap sites generated by these defects can capture the photogenerated carriers, leading to a reduction in photosensitivity. Additionally, the presence of unstable defects can introduce impurities such as oxygen and carbon, resulting in a degradation of photoresponsivity.

To enhance the photoresponsivity, it is necessary to develop a method that selectively passivates defects while preserving an active region. Previous research has explored the healing of defects through the adsorption of molecules with thiol groups. However, this approach is difficult to control using solution-based processes and raises concerns about contamination from residue solutions. In contrast, Atomic Layer Deposition (ALD) is a self-limiting process based on surface reaction that allows for precise control of film thickness, nanoparticle size, and coverage at the atomic level. ALD has proven highly effective for selective deposition on chemically reactive defects compared to basal planes. Additionally, the selective deposition of Pt, a representative noble metal, on defects is expected to introduce additional carriers to TMDCs via localized surface plasmon resonance (LSPR). However, there is a lack of research on the selective deposition of nanoparticles (NPs) on 2D TMDCs using ALD Pt.

In this study, we investigated a method for the selective deposition of ALD-based Pt NPs on WS_2, a promising photodetector material, with precise controllability at the sub-nanometer level. For the process development, dimethyl (N,N-dimethyl-3-buten-1-amine-N) platinum (DDAP) (TANAKA, Japan) was utilized as Pt precursors due to reduced steric hindrance resulting from small molecular structure, which allows for precise control of NP size. Specifically, we compared the growth characteristics of Pt NPs on the surfaces of 2D TMDCs based on the type of reactant. We obtained selectively deposited Pt on defects of the WS_2 substrate. Furthermore, we conducted in-depth research on the device performance and its influence based on the size and distribution of Pt NPs. The photocurrent of the Pt NP-functionalized WS_2 photodetectors was significantly higher than that of bare WS_2.

NS-MoP-11 Exploring the Challenges of Atomic Layer Deposition for Graphene Device Manufacturing, *Jaspreet Kainth*, *R. Coleman, R. Baines, H. Glass,* Paragraf, UK

Graphene has been speculated to be a suitable material for producing robust and sensitive Hall sensors and biosensors due to its ultra-high carrier mobility. A key challenge however is producing electronic grade, high mobility graphene at scale. Paragraf is the first company in the world to produce graphene using our proprietary and commercially scalable growth method, directly onto target substrates without the need of a transfer process, using standard semiconductor manufacturing tools.[1] We cover all aspects of production, from the growth of graphene to processing into final devices, resulting in the fabrication of Hall sensors and graphene-FETs.

Graphene is known to be sensitive to its surrounding environments, therefore the impact of the choice of materials, deposition methods and fabrication processes utilised during device manufacture must be well understood with respect to the final device performance. Paragraf employs the use of atomic layer deposition (ALD) as one of its methods for the fabrication of metal oxide thin films, which are required to integrate graphene into devices, since it is well established in producing high-quality films for applications such as high k dielectrics and encapsulation layers to improve device stability. It is well reported that ALD directly onto graphene is a challenge due to its lack of nucleation sites resulting in non-uniform coverage of films or even no film growth, which is a particular challenge for Paragraf due to our extremely low defect level, contaminant free graphene achieved via out particular growth methods. Therefore, development of metal oxide thin film growth via ALD onto graphene has not been trivial. In this work, we will discuss the routes explored to ensure the deposition of high-quality metal oxide films onto graphene, and the challenges with integrating such films into device fabrication processes. By tuning the metal oxide film properties, we have been able to control the final device performance allowing commercially viable devices to be successfully developed that meet our customers' requirements.

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NS-MoP-12 Atomic Layer Deposition Assisted Fabrication of Metal-Organic Framework Films for Flexible Biosensing Devices, *J. Wang, X. Ke, Z. Zhao,* Fudan University, China*; X. Zuo, **Xueqiang Lu**,* Jiangsu MNT Micro and Nanotech Co., Ltd., China*; G. Huang, Y. Mei,* Fudan University, China

Metal-organic framework (MOF) films possess considerable potential application in the field of biosensing devices due to their extensive surface area, abundant active sites, and high catalytic transition metal content. However, the controlled fabrication of MOF films for delicate devices and chips still presents numerous challenges, such as the issues of tight bonding with the substrate, controlled growth on complex substrates, and region-specific fabrication on the substrate. With an induction effect of oxide nanomembrane pre-deposited on substrate by atomic layer deposition (ALD), our group has achieved conformal, dense, uniform, and firmly bonded MOF films on both planar and 3D complex substrates (Figure S1) [1,2]. We then developed patterning techniques for MOF films: patterning the ALD oxide nanomembrane by photolithography enables the precise growth of MOF films with excellent regional selectivity and integration of MOF film into IC chip becomes available (Figure S1) [3,4]. Furthermore, we utilized this ALD assisted technology to prepare MOF film on water-soluble sacrificial layer, and then selectively remove the sacrificial layer, thus leading to preparation of large-area free-standing and transferrable MOF film for advantageous device on fragile substrate (Figure S2) [5]. We has specifically studied the induction effect of the ALD oxide nanomembrane and the growth mechanism of MOF films was disclosed. Several types of MOF films have been prepared by this general strategy, and were engaged in enzyme-free electrochemical biosensing. Due to the uniform and dense nature of the prepared MOF films, flexible biosensor devices towards glucose, lactic acid, dopamine, hydrogen peroxide, etc. with high sensitivities were demonstrated and the devices can be well attached to the human skin (Figure S3) [6-9]. The current ALD assisted approach opens a new window toward the preparation of high-quality MOF films and MOF film-based chips for advantageous sensing applications in post-Moore law period.

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NS-MoP-13 Growth of ALD Gold Nanoparticles on Oxide Surfaces, *Mari Napari*, *H. Cossey,* King's College London, UK*; A. Werbrouck,* University of Missouri*; J. Julin,* University of Jyväskylä, Finland*; S. Barry,* Carleton University, Canada*; A. Zayats,* King's College London, UK

Supported nanoparticles are used in a wide range of applications, including catalysis, photonics, and electronic devices such as sensors. All these applications require precise control of dispersion and size distribution of the nanoparticles for optimal performance, but scalable synthesis of size-selected nanoparticles on large-surface-area supports has proven to be challenging.Atomic layer deposition is often highlighted as a method to produce highly uniform ultra-thin films, but its potential in nanoparticle deposition has been given less attention. However, it has already been shown that ALD can be a viable technique for synthesis of noble-metal nanoparticles, with an option to control the growth by tuning the deposition parameters [1]. There are still remaining challenges in the more widespread use of ALD in nanoparticle synthesis, namely those related to the somewhat poor understanding of the nanoparticle growth and sintering mechanisms during the ALD process, and their dependence on the process parameters and support/substrate material.Here we investigate the use of ALD to grow gold nanoparticles. We use the 3-step ALD Au process developed by Griffiths et al.[2] with trimethylphosphinetrimethylgold, oxygen plasma, and water at 125C temperature. ALD Au nanoparticles are grown on different oxide surfaces, including SiO2, Al2O3, TiO2, and alkali-free glass. Particle sizes and size distributions are extracted from SEM and AFM images of samples with 25 - 400 ALD cycles, and the total number of Au atoms per unit area are measured using Rutherford backscattering spectrometry.

To understand the mechanisms of the ALD Au nanoparticle growth the acquired data are analysed using kinetic models, a population-balance model established by Grillo et al. [3], and a novel edge-growth nucleation model. With these models it is possible to distinguish between different nanoparticle growth regimes, where the nucleation of new particles and the evolution of the size distributions are dominated either by hetero/homogeneous reactions of the deposited gold with the substrate and already grown nanoparticles, or by surface diffusion and dynamic coalescence. This information can further be used to design new ALD-based size-selective nanoparticle synthesis processes.

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NS-MoP-14 Multilayered Thin Films for Solid Electrolyte Fabricated by Atomic Layer Deposition, *Xiang Yang Kong*, *A. Fiedler, X. Luo,* Shanghai Jiao Tong University, China*; S. Indris,* Karlsruhe Institute of Technology (KIT), Germany*; H. Ehrenberg,* Karlsruhe Institute of Technology, Germany

A novel multilayered thin-film solid electrolyte consisting of LiON-AlOx was synthesized by atomic layer deposition (ALD). The ALD-derived films were grown about 200°C on SiO2/Si substrate by an alternating deposition of lithium oxynitride (LiON) and AlOx sublayers with 1–6 nm thickness. The layer-by-layer structure of the films is observed using

cross-sectional HRTEM and confirmed by ToF-SIMS. The ionic conductivities of LiON-AlOx films are improved by doping with nitrogen in the Li-rich layers. From the electrochemical impedance spectra with elevated

temperature, the ionic conductivities of all multilayer LiON-AlOx films are increased by introducing heterointerfaces with enhanced conductivity along with these heterointerfaces. This is remarkable since the overall concentration of Li+ ions is lower in these heterostructures, compared to the single LiON film. An explanation for this behavior could be a high ion mobility at the interfaces, in analogy to layered structures of AlGaN/GaN where a high electron mobility at the interfaces due to the two-dimensional electron gas (2DEG). In this investigation, the increase of ion conductivity could be a result of the two-dimensional ion gas (2DIG) found at the interfaces.

Reference: X. Luo et.al., Solid State Ionics 373 (2021) 115796

ALD Applications
Room Hall 3D - Session AA1-TuM

Applications in ULSI BEOL: Interconnects, Diffusion Barriers, & DRAM

Moderators: Mike McSwiney, Applied Materials, **David Towner**, Intel Corp.

8:00am **AA1-TuM-1 Leakage Control of DRAM High-k Capacitor Stack by Ald Sc$_2$O$_3$, Y$_2$O$_3$ Inter-Layer**, *Randall Higuchi,* A. Babadi, C. Chen, B. Zope, Merck KGaA, Darmstadt, Germany

The scaling of DRAM devices and subsequent increase in memory density requires shrinking memory cell size, which necessitates engineering of the capacitor and transistor of the memory cell. Scaling of capacitor presents challenges in size shrink capacitor size and area shrinking, and reduction in number of stored charges. These factors contribute to increase in capacitor leakage, wherein it is critical to maintain leakage current $<10^{-7}$ A/cm^2 at the operating voltage [1].

ALD oxide films of Hf & Zr, when crystallized to non-monoclinic phase have high dielectric constant, and, therefore, utilized in the DRAM capacitor stack to achieve high capacitance. However, grain boundaries of these crystalline films form dominant carrier conduction paths leading to increased leakage current. Amorphous, thin ALD Al$_2$O$_3$ layer in the middle of the high-k stack is known to engineer grain boundary structure in the film creating tortuous carrier conduction path leading to lower leakage current [1]. In this work, we investigated alternate oxide materials for inter-layer that improve leakage performance of the capacitor stack compared to Al$_2$O$_3$ inter-layer. Our work demonstrated that ALD Sc$_2$O$_3$ or Y$_2$O$_3$ can be utilized as inter-layer in the DRAM high-k stack. ALD Sc$_2$O$_3$ resulted in 33% improvement and ALD Y$_2$O$_3$ resulted in 50% leakage current improvement compared ALD Al$_2$O$_3$ (deposited using trimethyl aluminum) inter-layer. Additionally, both Sc$_2$O$_3$ and Y$_2$O$_3$ inter-layer resulted in lower EOT increase compared to Al$_2$O$_3$.

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8:15am **AA1-TuM-2 ALD Deposited IGO with High Thermal Stability (~ 800 °C) by Controlling Crystallinity for Multi-bit Operation 2T0C DRAM**, *Jae-Hyeok Kwag,* S. Choi, J. Sim, T. Cho, C. Park, Y. Song, J. Park, Hanyang University, Republic of Korea

The 2T0C DRAM has advantages compared to conventional Si channel 1T1C in terms of high cell density (~ 6F^2), long retention time (> 400 s), and multi-bit operation using the current sensing mode [1-2]. Oxide semiconductors (OS) have advantages such as extremely low off current (< 10^{-18} µA/µm) [3]. Recently, capacitor-less 2T0C DRAM using a low off-current IGZO (In-Ga-Zn-O) channel was proposed. Since the FEOL fabrication includes a high-temperature process, high thermal stability is required to apply OS channel FET to DRAM. However, the electrical properties of the OS channel FET degraded above the 400 °C post-annealing process [4]. In general, Ga doping improves the thermal stability of OS. Among the various deposition methods for OS, atomic layer deposition (ALD) is a promising candidate because of its characteristics that allow easy doping concentration adjustment and easy sub-nanometer scale thickness control.

In this study, thermal stability (~ 800 °C) of Ga-doped InO channel FET was verified by controlling the thickness using the ALD method, and the 3-line based multi-bit operation of the 2T0C DRAM was confirmed. First, the InO channel FET was evaluated. The 250 °C deposited 3-nm thick InO using DBADMIn precursor was adopted to the channel layer. The c-axis aligned C(222) crystalline InO FET exhibits superior electrical properties by lowering the grain boundary effect [5] but degraded after 800 °C post-annealing for 3 hours, as shown in **Fig 1.**.To achieve high thermal stability, InO was doped with Ga using the ALD super-cycle method. The thickness of Ga-doped InO (IGO) was also evaluated because it is responsible for crystallinity. As shown in **Fig 2.**, Above the 10 nm thickness of the IGO channel, FET exhibits superior thermal stability even after the post-annealing process at 800 °C for 3 hours. The 800 °C post-annealed 10 nm thick IGO FET was adopted because the on-current and field-effect mobility were similar to 400 °C post-annealed InO channel FET (InO: 55.5 cm^2/Vs, IGO: 58.9 cm^2/Vs). As shown in **Fig 3.**, the current sensing multi-bit operation is exhibited regardless of channel material, and the RBL current has similar values according to the WBL voltage because the mobility is similar with InO and IGO channel FET.

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8:30am **AA1-TuM-3 Improving Electrical Properties of ZrO$_2$ Dielectric Films Without Sacrificing Tetragonal Crystallinity via Gd Doping**, *Seungwoo Lee, Y. Choi, J. Jeong, J. Nam,* Kyung Hee University, Republic of Korea*; H. Oh, H. Kim, Y. Park,* SK trichem, Republic of Korea*; W. Jeon,* Kyung Hee University, Republic of Korea

ZrO$_2$ has been used as an insulator film for dynamic random-access memory capacitors for a long time due to its compatibility with TiN electrodes and the high maturity of the atomic layer deposition (ALD) process. Tetragonal ZrO$_2$ thin films with a high dielectric constant (~40) on TiN electrodes could be obtained relatively easily by ALD. However, there are limitations to using only ZrO$_2$ due to the leakage current problem. The inevitably present grain boundaries acted as the dominant carrier conduction path. Al-doped ZrO$_2$ effectively suppressed leakage current by reducing the grain size and inducing a winding conduction path, but it also caused the crystallinity of ZrO$_2$ to deteriorate. Therefore, further scaling requires new dopants that can replace the role of Al without sacrificing the tetragonal crystallinity of ZrO$_2$.

In this regard, this presentation discusses the results of employing Gd as a dopant to replace Al. The Gd$_2$O$_3$ ALD process for doping in ZrO$_2$ was designed utilizing a novel Gd precursor. We investigated the effectiveness of Gd as a dopant for ZrO$_2$ by fabricating metal–insulator–metal capacitors with Gd-doped ZrO$_2$ as an insulator film and analyzing its electrical properties. As the ratio of Gd$_2$O$_3$ in the dielectric increased, the capacitance density decreased, but the leakage current characteristics were noticeably improved. Furthermore, as a result of analyzing the crystallinity of the Gd-doped ZrO$_2$ thin film by X-ray diffraction analysis, it was found that Gd doping did not significantly deteriorate the tetragonal crystallinity of ZrO$_2$.

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8:45am **AA1-TuM-4 Area Selective Co ALD for Highly Reliable ULSI Interconnect System and the Establishment of ALD Process Design Framework**, *Yukihiro Shimogaki,* The University of Tokyo, Japan   **INVITED**

As ULSI becomes more highly integrated, the current density flowing through Cu multilevel interconnects increases, and it has become difficult to ensure device reliability owing to the emergence of wire breakage defects caused by electromigration. In addition, device performance degradation owing to RC delays is a major problem. To solve these issues, it is essential to form a liner layer with a material that exhibits good adhesion to Cu, suppresses electromigration, and crowns the Cu line with a metal cap during the damascene process. It is also important to increase the proportion of Cu in ultrafine Cu interconnects and reduce the effective resistance by employing a thin barrier metal with high Cu diffusion barrier properties.

To address these issues, we have reported that CoW alloy thin films synthesized by ALD have better Cu diffusion barrier properties than existing TaN and higher adhesion to Cu than Ta. We have also shown that Co can be selectively formed on the Cu surface by combining ALD and ALE, and can be used as a metal cap layer.

In this presentation, we report the results of the evaluation of the Cu diffusion barrier properties of CoW films and the development of an AS-ALD process for Co films. To develop an efficient AS-ALD process, we introduce a method to search for novel precursor compounds with appropriate vapor pressures, and a method to estimate and measure the adsorption equilibrium constants of the precursor candidates. We also introduce a method for in situ observation of the incubation cycle by reflectance spectroscopy of the growth surface, and report the results of our investigation of growth conditions and surface treatment methods that exhibit selectivity. These methods are summarized to establish a framework for the ALD process design.

Figure 1 shows the Co film growth on SiO$_2$ by ALD and ALD/ALE combination. CCTBA (Dicobalt hexacarbonyl tert-butyl-acetylene) was employed as the Co precursor, and a sequential supply of SO$_2$Cl$_2$ and HFAC

was used for Co-ALE. Co-ALE was effectively remve the small nuclei formed on the SiO_2 during Co-ALD, which can be used to enhance the selectivity of Co AS-ALD. Figure 2 shows the leakage current of the L/S pattern electrodes with Co-ALD, Co-ALD with HMDS pretreatment, Co-ALD with HMDS pretreatment and ALE combination. Co-ALE and HMDS pretreatments effectively suppressed unwanted nucleation on SiO_2, while Co thin films were selectively grown on the Cu surface.

9:15am AA1-TuM-6 Atomic Layer Deposition (ALD) of Transition Metal Dichalcogenides (TMDS) Layers as Metal Diffusion Barriers for Back-End-of-Line (BEOL) Applications, *A. Mane,* Argonne National Laboratory*; S. Katta, J. Morris, C. Phatak,* **Jeffrey Elam,** Argonne National Laboratory, USA
The aggressive pursuit of miniaturization in microelectronics has led to a significant reduction in the size of individual device features, consequently boosting device density on chip. This heightened density necessitates more metal interconnect wirings, which, in turn, requires a reduction in wiring dimensions and an increase in the aspect ratio of vias and trenches [https://irds.ieee.org/]. As a result, existing metal lines, typically composed of copper and a liner acting as a diffusion barrier, must undergo proportional shrinking. Scaling down the barrier layer creates a relatively larger volume for copper, effectively keeping resistivity low. However, conventional Ta/TaN thin barriers may exhibit poor performance below 3nm and eventually fail. Therefore, there is substantial interest in exploring new metal diffusion barrier materials, such as two-dimensional Transition Metal Dichalcogenides (2D-TMDs) which hold promise for serving as effective diffusion barriers at smaller thicknesses and layered structured [Deijkers *et al*., Adv. Mater. Interfaces 2023, 10, 2202426].

Here, we present our recent work on thermal low-temperature (200-400℃) ALD of MX_2 layers including MoS_2, HfS_2, and TaS_2. The ALD of these layers was investigated using in-situ quartz crystal microbalance (QCM) and spectroscopic ellipsometry measurements. Following optimization of the ALD processes, we applied ultrathin layers (4-10nm) of MoS_2, HfS_2, and TaS_2 on Si, SiO_2, and SiN wafers. Subsequently, MOS-type devices were fabricated by depositing 50nm thick copper dots using the sputtering deposition. These MX_2-intigrated MOS devices underwent testing via time-dependent dielectric breakdown (TDDB) measurements. The time-to-breakdown of structures under high electric field stress conditions and failure time were examined as functions of thickness and MX_2 layer chemistries. In addition to TDDB studies, the barrier properties of the MX_2 layers were evaluated using the standard buffer oxide etch (BOE) test. Various types of MX_2-based MOS structures were dipped in a BOE solution, and the etch rate of SiO_2 and SiN was determined and correlated to MX_2 chemistry. This wet etch test study is crucial for evaluating material stability, particularly concerning Cu metal adhesion and chemical stability, which are pertinent during the chemical mechanical planarization (CMP) process. Based on the obtained results, we underscore the potential of ALD for implementing 2D-TMD barriers in BEOL metallization applications.

9:30am AA1-TuM-7 High-Quality Co Thin Film by Thermal ALD Using CCTBA Precursor by Controlling H_2 Dose, *Jun Yamaguchi,* N. Sato, A. Tsukune, T. Momose, Y. Shimogaki, The University of Tokyo, Japan
With the scaling of semiconductor integrated circuits, RC delay and power consumption have increased owing to higher line resistance, and reliability degradation due to electromigration (EM) has become a problem. The use of cobalt (Co) in interconnect layers has attracted attention as a solution to these issues. Co liner, Co cap, and Co interconnects replacing Cu, are expected to address these challenges. For these applications, it is necessary to form high-quality, low-resistance Co ultrathin films uniformly on both the macroscale (entire wafer) and microscale (via, trench). Therefore, the use of atomic layer deposition (ALD) is desirable. From the perspective of substrate damage and step coverage, thermal ALD is preferable to plasma-enhanced ALD. However, the chemical options available for thermal ALD are limited. For instance, while there have been reports of Co-ALD utilizing the $Co(DAD)_2$ precursor,[1] the issue arises from $Co(DAD)_2$ being a solid with a low vapor pressure. In contrast, CCTBA is a highly volatile liquid and an appropriate Co precursor. Therefore, in this study, we focus on the thermal ALD of Co using CCTBA.

Hot-wall ALD equipment was used for Co deposition. CCTBA and H_2 were used as the precursor and reactant, respectively, and N_2 was used as the carrier and purge gases, respectively. CCTBA was vaporized at 45℃ and bubbled with the carrier gas. The chamber temperature was maintained at 100℃. A sputtered Cu film was used as an underlayer. The composition of the Co film was measured using XPS, and the film thickness was determined using SEM.

Figure 1 shows the growth per cycle (GPC) of the Co film according to the CCTBA supply time. The GPC became saturated after 5 s, and the saturated GPC (0.05 nm/cycle) was smaller than the Co monolayer thickness (0.2 nm). This suggests that the deposition was self-limited via the surface saturation of the adsorbing precursors, which is typical of ALD. Figure 2 shows a cross-sectional SEM image of the Co film deposited on a Si trench structure with an aspect ratio of 8.4. Conformal deposition, a feature of ALD, has been achieved. Figure 3 shows the composition of the Co film versus the H_2 dose. As the H_2 dose increased, the amount of carbon impurities decreased, and the film purity improved. Figure 4 shows the XPS results for the Co film deposited under high H_2 supply conditions. No peaks of C and O, which were present in the CCTBA precursor, were observed, indicating the successful deposition of a high-quality Co film. The Co film resistivity was measured to be 27 μΩ·cm with a thickness of 36 nm.

9:45am AA1-TuM-8 Improved Properties of Atomic Layer Deposited Ru Films by Providing Additional Reactant for Cu Alternative Interconnects, *Jeongha Kim,* K. Sang Bok, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; T. Cheon,* Daegu Gyeongbuk Institute of Science & Technology (DGIST), Republic of Korea*; S. Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea
Ru emerges as a next-generation interconnect materials capable of overcoming the scaling limits encountered with Cu interconnect [1]. Generally, as the deposition temperature increases, the properties of metal thin films deposited by ALD improve due to the grain size increase and impurities reduction by the enhanced chemical reaction. But at deposition temperatures where the precursor thermal stability isn't ensured, its thermal decomposition occurs, leading to degraded in thin film properties such as increased resistivity owing to the significant impurities and retarded grain growth. In this study, a novel ALD-Ru process has been developed, which provides additional reactant followed to obtain high-performance ALD-Ru process capable of maintaining excellent properties, even at temperatures where precursor thermal decomposition happen. Here, a Ru metalorganic precursor, tricarbonyl(trimethylenemethane)ruthenium $[Ru(TMM)(CO)_3]$ was used for ALD-Ru. It was reported that by using this precursor, a high-quality film with a very low resistivity (~12.9 μΩ·cm) was obtained in ALD temperature window (260℃)[2]. But, the precursor thermal stability has been kept to ~260℃ and at 275℃, the thermal decomposition of the precursor started and the resistivity of the film deposited at 300 ℃ was again increased due to the incorporation of carbon impurity. In this study, to improve the properties of Ru thin film, ALD-Ru process was done at higher deposition temperature at 310℃. Moreover, to remove contamination of the film resulting from the precursor thermal decomposition, NH_3 has been provided as an additional reactant followed by providing the main counter reactant, O_2, which is called 6-step ALD process (figure 1). Thus, when only O_2 was used (4-step ALD), the GPC was as high as ~2.4 Å/cycle and with the additional injection of NH_3, the GPC decreased to ~1.3 Å/cycle. The resistivity of the film was as high as 20.1 μΩ·cm using a conventional 4-step process but with 6-step process, is was decreased to ~13.6 μΩ·cm. In addition, an increase in peak intensity was confirmed through XRD analysis (figure 2), indicating the improvement of the film crystallinity by 6-step ALD process. An ALD-Ru film with a thickness of 26 nm was obtained with an excellent physical and compositional conformality and nearly 100% step coverage at the hole feature with a high aspect ratio of ~25. In summary, 6-step ALD-Ru process to supply additional reactant followed by the main counter reactant can provide the valuable process option to obtain the high-quality metal film at higher deposition temperature where the precursor thermal decomposition.

ALD Applications
Room Hall 3D - Session AA2-TuM

Energy: Solar Energy Materials I
Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., **Nathanaelle Schneider**, CNRS-IPVF

10:45am AA2-TuM-12 ALD Layers and Interfaces in Next Generation Photovoltaics, *Mariadriana Creatore,* TU Eindhoven, Netherlands **INVITED**
Innovation in thin film and interface engineering has played an essential role in pushing the conversion efficiency of the most widespread photovoltaic (PV) technology, i.e. crystalline silicon-based (c-Si), towards its thermodynamic limit. In this respect, ultra-thin, conformal, high-purity Al_2O_3 thin films synthesized by ALD are key in c-Si PV manufacturing industry as they passivate the c-Si surface, thereby suppressing a major channel of electron-hole pair recombination.

Recently, we have explored the ALD synthesis of thin films for metal halide perovskite- based photovoltaics. The latter has rapidly reached a conversion efficiency of 26% and, when coupled with c-Si PV in a so-called tandem device, leads to efficiencies already beyond 33%.

In this contribution I will discuss the merits which ALD offers to perovskite-based PV by reviewing our work on NiO-based hole transport layers and discussing in depth the case study of ALD SnO_2. The latter is implemented in perovskite PV R&D and industry as buffer layer, i.e., imparting thermal and environmental stability to the device, while protecting the perovskite absorber and fullerene electron transport layer from the sputtering of the transparent top contact. More recently, ALD SnO_2 is explored as solvent barrier layer in the tunnel recombination junction of perovskite/perovskite tandem PV, to prevent the damage of the wide-gap perovskite absorber when processing the narrow band-gap perovskite cell. Although we can conclude that several ALD merits are already extensively acknowledged by the PV community, studies addressing ALD film growth on challenging substrates such as fullerenes and metal halide perovskites are rarely reported in literature. We are convinced that these studies provide a rationale to implement more efficiently these layers at device level and promote process upscaling. Therefore, this contribution will also highlight the adoption of *in situ* diagnostics, namely spectroscopic ellipsometry and IR spectroscopy, to characterize the ALD SnO_2 growth on two commonly adopted fullerenes, C60 and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Our studies show that a substrate-inhibited growth occurs in the case of PCBM and, to a minor extent, in the case of C60, with respect to the traditional c-Si substrate. Moreover, IR spectroscopy highlights the loss of vibrational features of the ester group in PCBM upon SnO_2 growth, whereas C60 is chemically unaffected. We conclude that the delayed film growth and chemical modifications detected on PCBM are responsible for the consistently lower device performance when ALD SnO_2 is grown on PCBM instead of C60.

11:15am AA2-TuM-14 Utilizing Low-Temperature Ald Technique to Investigate Perovskite Nickelates for Photovoltaic Applications, *Anjali Choubey, H. Hovde Sønsteby,* University of Oslo, Norway*; H. von Wenckstern,* University of Oslo, Germany*; O. Nilsen,* University of Oslo, Norway

Photovoltaic (PV) materials currently in use like silicon are well-established but approaching their theoretical limit, and halide-perovskites, even though developing rapidly, are toxic and unstable under environmental conditions. Developing new materials for PV applications is slowly becoming a crucial necessity. In this study, perovskite nickelates are investigated as an alternative to traditional PV materials. Nickelates are not only stable under environmental conditions, but they can also withstand photobleaching and thermal exposures. Additionally, they are well known for their metal-insulator phase transition, magnetic phase transition, and structural transition [1, 2]. This has made them very lucrative for various electronic, magnetic, dielectric, superconducting, and catalytic applications. However, there is not much data on the use of nickelates for PV applications, and we are trying to bridge that gap.

Some perovskite nickelates have shown bandgap tuning abilities by A-site substitution control [2-4]. In this work, Terbium nickelate ($TbNiO_3$) and Gadolinium nickelate ($GdNiO_3$) thin films fabricated using low-temperature atomic layer deposition (ALD) techniques were studied and characterized. X-ray diffraction gave information about the structure and crystallinity, x-ray fluorescence and x-ray photoelectron spectroscopy about the composition, and spectroscopic ellipsometry about the thickness and refractive indices of the deposited films. These investigations helped gain valuable insight into the extent of the semiconductive nature of these materials and how to exploit them for PV applications.

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11:30am AA2-TuM-15 Atomic Layer Deposition of Defect-Engineered TiO_x and TaO_x Protective Coatings for Photoelectrochemistry, *Tim Rieth, O. Bienek, J. Kühne, I. Sharp,* Walter Schottky Institut, Technische Universität München, Germany

Photoelectrochemical (PEC) energy conversion provides a viable route to chemical fuel production from solar light. In this approach, charge carriers generated within a semiconductor light absorber immersed in an electrolyte are used to drive electrochemical reactions. Several different PEC design approaches exist, ranging from single photoelectrodes to tandem configurations of photoanodes and -cathodes to buried photovoltaic junctions. However, common to each of these designs is a central materials challenge of achieving simultaneous stability, efficiency, and scalability. Furthermore, the coupling of the semiconducting photo absorber and catalytic components demands sophisticated solid state interface engineering. In this talk, we focus on the stabilization of this semiconductor/electrolyte interface with functional conformal coatings grown by plasma-enhanced atomic layer deposition (PE-ALD). We investigate defect-engineered electron-selective titanium oxide (TiO_x) protection layers for efficient InP photocathodes and identify ALD pathways to optimize interfacial and bulk charge transport, as well as to tune the driving force for photovoltage generation [1, 2]. Furthermore, we use PE-ALD to deposit ultra-thin tantalum oxide (TaO_x) protective coatings showing improved chemical stability compared to TiO_x in alkaline and acidic environments. We extend the utilization of TiO_x and TaO_x protective coatings to buried photovoltaic junctions and evaluate the respective suitability in terms of optical transparency, conductivity and stability, achieving unassisted solar-water-splitting efficiencies of 15%. Spectroscopic methods, including X-ray photoelectron spectroscopy (XPS), photothermal deflection spectroscopy (PDS), and spectroscopic ellipsometry (SE), are employed to characterize and understand the intentionally introduced defects and correlate electronic properties to the PEC performance. Overall, the presented TiO_x and TaO_x protective coatings represent an important step toward efficient and stable PEC devices, while the demonstrated ALD-based defect engineering generally enables electronic property control of ultra-thin layers.

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11:45am AA2-TuM-16 Influence of Atomic Layer Deposition Tin Oxide Properties on the Performance of Perovskite Solar Cells, *Bhavya Rakheja, A. Hultqvist,* Uppsala University, Angstrom Laboratory, Sweden*; T. Törndahl,* Uppsala University, Sweden

Presently, the photovoltaic industry is dominated by single-junction silicon solar cells. As this technology is reaching its theoretical power conversion efficiency limit, the need to develop multi-junction solar cell structures, capable of producing more power per unit area, is rising. Multi-junction solar cells employ a combination of single-junction solar cells, each capable of absorbing complementary parts of the solar cell spectrum. Perovskite solar cells (PSCs) have witnessed tremendous success and their efficiency has improved from merely 3.8% in 2009 to more than 26% in a single-junction solar cell [1]. Moreover, PSCs have also demonstrated great efficiencies when used in tandem configurations with silicon and Copper indium gallium (di)selenide (CIGS) solar cells [1]. All top efficiency PSCs in a tandem structure employ tin oxide (SnO_x), grown using the Atomic layer deposition (ALD) technique, as an electron selective buffer layer. *The material properties of SnO_x are crucial for facilitating good electron transport while mitigating losses.*

The perovskite layer in a PSC is sandwiched between electron and hole-selective layers. These layers facilitate the transport of the generated charge carriers to their respective contacts. Good energetic alignment between perovskite and charge transport layers is pivotal in maximizing the solar cell's power output. As it has been established in several studies, the bandgap of ALD SnO_x is sensitive to the deposition temperature [2]; making it critical to optimize the band alignment between ALD SnO_x and adjacent layers. Moreover, other process parameters such as the choice of co-reactant can also affect the number of defects and; consequently, impact the power losses in a PSC [3]. In this study, we conduct in-situ quartz crystal microbalance studies and also investigate how the material, optical, and electronic properties of ALD SnO_x evolve as a function of deposition parameters, and their influence on solar cell's device parameters. In particular, we examine the effect of two co-reactants (H_2O and H_2O_2) and their respective doses. By fine-tuning ALD SnO_x deposition parameters and studying their influence on the device performance, one can establish an improved understanding toward the incorporation of ALD SnO_x in PSCs.

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ALD Fundamentals
Room Hall 3A - Session AF1-TuM

Precursors and Chemistry: Precursor Design, New Precursors, Process Development II

Moderators: Hyungjun Kim, Yonsei University, Korea, **Atsushi Sakurai**, ADEKA CORPORATION

8:00am AF1-TuM-1 Navigating the Semiconductor Market for ALD Precursors - in the Past and in the Future, *Jonas Sundqvist,* TECHCET LLC CA, Germany

The semiconductor industry has been witnessing more than two decades of high volume scale up in the production and application of ALD and CVD precursors, particularly within Advanced Logic, DRAM, and 3DNAND sectors. Recent research by TECHCET reveals a nuanced landscape where the ALD/CVD precursor market, after a period of stagnation in 2023 due to declining memory pricing, is poised for a significant resurgence. This expected revival is attributed to the recovery in memory pricing and a robust demand for metal, high-κ and low-κ dielectric precursors, essential for the fabrication of advanced semiconductor devices.

The research underscores a dynamic growth trajectory for ALD/CVD precursors, driven by the expansion of leading-edge logic devices and the transition of DRAM to more sophisticated Multi Patterning and Extreme Ultraviolet (EUV) technologies. Moreover, the ongoing scaling of 3DNAND architectures to beyond 500 layers heralds an increased demand for several high volume precursors, essential for high aspect ratio etch and deposition processes. This demand is further amplified by the full implementation of High-k/Metal Gate technologies also in DRAM, necessitating a steady supply of hafnium precursors despite existing supply chain challenges.

Notably, the supply dynamics of critical materials like tungsten, derived from WF6 precursors, integral to the vertical scaling of 3DNAND, indicate a balanced supply-demand scenario through 2023, with potential constraints anticipated by 2026. This looming shortage underscores the semiconductor industry's relentless pursuit of alternative materials and processes, such as the potential adoption of molybdenum solid precursors, to ensure the sustainable growth of ALD/CVD precursor markets.

This research encapsulates the resilience and adaptability of the semiconductor industry, highlighting the critical role of ALD/CVD technologies in meeting the ever-increasing demands for higher performance and more compact semiconductor devices. The anticipated growth in the ALD/CVD precursor market not only reflects the industry's response to current challenges but also its proactive stance towards future technological advancements. A deeper dive into historical IÅP filing by Fabricators, Equipment companies and precursor suppliers will be given.

8:15am AF1-TuM-2 Improvement of COSMO-SAC Method for Estimating Vapor Pressure of ALD Precursors, *Noboru Sato,* The University of Tokyo, Japan*; Y. Wu,* The University of Tokyo, Japan, China*; J. Yamaguchi, A. Tsukune, Y. Shimogaki,* The University of Tokyo, Japan

In ALD, metal complexes (MCs) are mostly used as precursors. Because a sufficient concentration of the precursor is necessary for saturated adsorption, MCs with high vapor pressures are required. Therefore, a method to accurately predict vapor pressure is required when designing new precursors for ALD. In this study, the vapor pressure prediction of MC using COnductor-like Screening MOdel Segment Activity Coefficient (COSMO-SAC) method[1] was investigated.

Vapor pressure calculations using COSMO-SAC method were performed using Amsterdam Modeling Suite[2]. The existing COSMO-SAC method can predict the vapor pressure of MCs with CO or cyclopentadienyl groups with double or half the accuracy of COSMO-SAC method, which is sufficient for precursor selection. However, the vapor pressures of MCs with β-diketonate, amidinate, and alkoxide groups were underestimated by a factor of 100–1000. Therefore, the conventional COSMO-SAC method cannot be applied to a wide range of precursor selection methods.

To improve the accuracy of vapor pressure estimation, we added three procedures to the conventional COSMO-SAC method. Figure 1 shows a schematic of the conventional COSMO-SAC method (black arrows) and improved COSMO-SAC method (colored arrows). As there are no ε_{dsp} (empirical parameters to calculate dispersive interactions) data for metal atoms, we investigated the non-regressive method to calculate ε_{dsp} (blue arrows in Fig 1). Because the dispersion force is known to be correlated with polarizability, we predicted that ε_{dsp} would also be correlated with polarizability. We found a correlation between ε_{dsp} and polarizability, expressed by the following equation:

$\varepsilon_{dsp} = 1035 \times \alpha^{1.34}$,

where α is the polarizability of the atoms in the molecule. By calculating the α of the metal atom in the MC and substituting it into this equation, we estimated the ε_{dsp} of the respective metal atoms. Then, we modified the activity coefficient due to dispersion interactions (γ_{dsp}) based on the polarizability of molecules (red arrows in Fig 1) and branching in the molecules (green arrows in Fig 1).

Figure 2 shows the measured vapor pressure of titanium tetraisopropoxide (TTIP) and those estimated using our method and the conventional method. Our method reproduced the experimental values more accurately than the conventional method did.

Figure 3 shows a comparison between the experimental and estimated vapor pressures of various MCs. As shown in Fig 3, our method reproduces the vapor pressure with an accuracy of approximately 50–200%, which is sufficient to determine whether the MC is suitable for ALD.

8:30am AF1-TuM-3 ALD Young Investigator Award Finalist Talk: Development of Precursors and Reactivity for Thermal Atomic Layer Deposition (ALD) of Main Group Elements, *Majeda Al Hareri, D. Emslie,* McMaster University, Canada

The majority of the developments in elemental ALD have involved transition metals. However, interest in main group ALD has increased in recent years due to potential applications in a variety of technologies.[1-3] Research in the Emslie group is focused on the design, synthesis, and characterization of new precursor molecules, and investigations into their use as thermal ALD precursors through a combination of solution-state reactivity studies and ALD reactor studies. Through modification of the precursor design of a previously reported elemental antimony ALD process,[4] we recently developed the first example of room-temperature thermal ALD of a pure element, using $Sb(SiMe_3)_3$ in combination with $SbCl_3$ to grow pure antimony films on H-terminated Si and SiO_2 substrates.[5] Efforts to expand this research to elemental boron ALD will be described, including synthesis of the potential precursors, $(R_3E)_2B(NR'_2)$ (E = Si or Ge), spectroscopic and crystallographic characterization of these compounds, and attempted boron deposition using a boron trihalide (BX_3; X = Cl, Br) co-reactant; anticipated byproducts in this reactivity are R_3EX and $B(NR'_2)X_2$, where the formation of strong E–X bonds provides a thermodynamic driving force. Development of a thermal ALD process for elemental germanium will also be described, achieving self-limiting growth at relatively low temperatures, and exhibiting substrate selectivity for deposition on H-terminated Si rather than SiO_2.

References

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8:45am AF1-TuM-4 A New ALD Process for Elemental Tellurium, *Paavo Porri, T. Hatanpää, H. Nieminen, K. Mizohata, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Research on ALD of metal tellurides has been focused on phase-change memory materials. Owing to their electrical switching behaviour, binary and

ternary compounds and alloys of germanium, antimony and tellurium have become an important area of development for memory and selector devices. Elemental tellurium has also garnered interest in materials research due to its thickness-dependent electrical properties, air stability and high hole mobility. Thus, it has been found to be a potential candidate to ensure continuing the miniaturization of transistors. However, process studies for depositing tellurium films are quite scarce. This study aims to illuminate a new ALD chemistry route for elemental Te films by combining an alkylsilyl telluride precursor with tellurium dichloride. In addition to elemental Te films, the new ALD process can be used for tuning the composition of metal telluride compounds such as GeTe.

The depositions were done in a commercial flow type ALD reactor using $(Et_3Si)_2Te$ (bis(triethylsilyl) telluride) and $TeCl_2$ as precursors. The process is expected to involve a dechlorosilylation reaction, which follows the Lewis hard-soft acid-base principle. Film morphology was studied with SEM, film crystallinity and crystallization temperature with XRD, and elemental composition with ToF-ERDA. Tellurium growth was observed at a temperature range of 90-110 °C. Film morphology and growth rate were highly dependent on the substrate. On native silicon oxide, the nucleation was sparse, and morphology of the deposited material initially resembled nanowires that subsequently coalesced with further deposition cycles. On Au the film morphology was smoother and continuous already at low cycle numbers. The considerable difference in the growth rates between native SiO_2 and Au is leveraged to attain area selective growth on Au. The films deposited in mild conditions are crystalline exhibiting hexagonal crystalline structure, and of high purity. A GeTe ALD process was modified with the studied Te process to yield tellurium-rich Ge_xTe_y films with enhanced phase transition temperature.

9:00am AF1-TuM-5 Development of an Innovative Method to Find New Efficient Gallium ALD Precursors, *Eva Pugliese, D. Coutancier, J. Hervochon, P. Pavard,* CNRS-IPVF, France*; C. Gosmini,* Ecole Polytechnique - CNRS, France*; V. Lair,* Cimie ParisTech PSL, France*; A. Ringuede,* Chimie ParisTech PSL, France*; M. Bouttemy,* Institut Lavoisier de Versailles, France*; A. Auffrant,* Ecole Polytechnique - CNRS, France*; N. Schneider,* CNRS-IPVF, France

Atomic Layer Deposition (ALD) is a booming technology to deposit thin films and it has been applied in several fields. This technique is based on surface-chemical reactions, and relies on the gas phase transport of metal containing molecules into a reaction chamber. However, not any molecule is suitable to be used as precursor, as they must be thermally robust while being sufficiently volatile and chemically labile to react with the surface functional groups. Organometallic chemistry offers a nearly infinite set of options to design new efficient precursors, though predicting their volatility and reactivity in the ALD chamber remains a challenge.[1] Establishing an efficient method to assess the physical and chemical properties of complexes would grant access to new ALD precursors and a better understanding of surface reactions.

This communication focuses on the development of new efficient gallium precursors to be used in the ALD of oxygen-free gallium-containing sulfide thin films.[2] A series of gallium complexes with chelating nitrogen based ligands (guanidinate, amidinate and triazenides) were synthesized and characterized (NMR, XRD) thanks to modular procedures.[3,4] To assess the thermal stability of the reagents and shed light on their transport in ALD, thermal analysis (TGA,DSC) were realized under N_2 and vacuum to mimic transport conditions. Finally, reactivity studies in solution of established ALD precursors and synthesized complexes provide an insight of surface reactions, which might take place in an ALD chamber. Having selected the most promising candidates, they were tested for film growth in an ALD apparatus using QCM setup. Interestingly, it was possible to highlight the crucial role of the non-chelating ligands in the film growth. Complexes with methyl ligands lose their surface reactivity after few cycles, whereas their substitution with amino groups can give a constant GPC over the whole range of the study. Gallium sulfide thin film could be prepared and their chemical fine composition was analyzed by XPS.

These results display the challenges that we may encounter in the targeting of new precursors and the importance of establishing a precise method to predict reactivity in ALD conditions.

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9:15am AF1-TuM-6 Atomic Layer Deposition of Co₂P Thin Films, *Elisa Atosuo, P. Deminskyi,* ASM Microchemistry Ltd., Finland*; K. Mizohata, T. Hatanpää, M. Ritala,* University of Helsinki, Finland

In this work we have deposited cobalt phosphide (Co_2P) by thermal ALD. Co_2P is a metallic material that has potential in a variety of applications such as hydrogen evolution reaction and lithium-ion batteries.

In general, the ALD processes for metal phosphides are scarce and mostly use the highly toxic PH_3 gas as the phosphide source. To our knowledge, only two ALD processes for transition metal phosphides has been reported. CoP_x has been deposited using $Co(AMD)_2$ with PH_3 plasma and H_2 plasma as precursors.[1] MoP was deposited by using $MoCl_5$ and PH_3.[2]

In this work Co_2P was deposited by using $CoCl_2$TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) and tris(trimethylsilyl)phosphine ($P(SiMe_3)_3$) as precursors. Alternatively, Co_2P can be deposited by using a three-precursor process: $CoCl_2$(TMEDA), NH_4F and $P(SiMe_3)_3$. The advantages of our processes are that we avoid the use of toxic PH_3 but also the possible damage caused by plasma.

Co_2P films were deposited with the $CoCl_2$(TMEDA) + $P(SiMe_3)_3$ process at 225–250 °C. The GPC was approximately 0.65 Å at 250 °C. Saturation of the GPC with respect to both precursors was verified at 250 °C. The films consist of orthorhombic Co_2P as measured by XRD, and the Co/P ratio is close to 2 as measured by ToF-ERDA. The main impurity is carbon, decreasing with the decreasing deposition temperature from 9.5 at-% at 250 °C to 6.7 at-% at 225 °C. However, with the three-precursor process lower deposition temperatures can be used and the C content is lower, e.g., ~ 3.3 at-% at 215 °C. In addition, only a small F content (e.g. ~0.4 at-%) was found in the films.

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9:30am AF1-TuM-7 The Effect of Co-Reactants on Interfacial Oxidation in Atomic Layer Deposition of Oxides on Metal Surfaces, *J. Swarup, H. Chuang, A. You, James Engstrom,* Cornell University

We have examined the ALD of Al_2O_3 using TMA as the precursor and *t*-BuOH and H_2O as the co-reactants, focusing on the effects of the latter on both the ALD process and the possible modification of the underlying substrate. We have employed a quartz-crystal microbalance (QCM) to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized using X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and X-ray reflectivity. Growth of thin films of Al_2O_3 using TMA and either *t*-BuOH or H_2O as the co-reactant at T = 285 °C produces thin films of similar physical properties (density, stoichiometry, minimal carbon incorporation), and the growth rate per cycle is similar for the two co-reactants at this temperature. At a lower temperature of T = 120 °C, the behavior is starkly different, where growth occurs with H_2O but not with *t*-BuOH. At either process temperature, we find no evidence for significant coverages of a long-lived *tert*-butoxy species from the reaction of *t*-BuOH. Deposition of thin films of Al_2O_3 on metal surfaces of Cu and Co has been examined for evidence of interfacial oxidation. While growth with either co-reactant does not lead to the oxidation of the underlying Cu substrate, use of H_2O leads to the oxidation of Co, while use of *t*-BuOH as the co-reactant does not. Thermodynamic factors may affect early stages of growth as Al species will likely scavenge all free O species. In contrast, at later times diffusion of species through the deposited Al_2O_3 thin film could result in oxidation at the Al_2O_3|metal interface, a process that is strongly hindered in the case of *t*-BuOH due to its size. This observation highlights the importance of the choice of the co-reactant concerning ALD of oxides on metal surfaces.

ALD Fundamentals
Room Hall 3A - Session AF2-TuM

Growth and Characterization: Plasma Enhanced ALD I

Moderators: Hyeontag Jeon, Hanyang University, **Erwin Kessels**, Eindhoven University of Technology, Netherlands

10:45am **AF2-TuM-12 Plasma-Enhanced ALD of Ga$_2$O$_3$ and Gan with Remote CCP-Plasma, Short Cycle Times, and Substrate Biasing**, *Roel Theeuwes*, Eindhoven University of Technology, Netherlands; *L. Gutmann*, Eindhoven University of Technology, Germany; *H. Knoops*, Oxford Instruments Plasma Technology, Eindhoven University of Technology, Netherlands; *E. Kessels*, Eindhoven University of Technology, Netherlands

The unique merits of atomic layer deposition (ALD), including high uniformity, high conformality, and excellent thickness control, often come with the caveat of relatively long processing times. Therefore, there is a demand for faster ALD processing, which has driven innovations in terms of ALD reactor and plasma source design.[1] In this work, we investigate plasma-enhanced ALD (PE-ALD) of gallium oxide (Ga$_2$O$_3$) and gallium nitride (GaN) on a new ALD system, designed for ultrafast and low-damage PE-ALD processing with rf substrate biasing capabilities. Ga$_2$O$_3$ and GaN are materials with highly suitable properties for use in various applications, including power devices.[2,3]

The PE-ALD processes for Ga$_2$O$_3$ and GaN were developed on an Oxford Instruments PlasmaPro ASP and serve to further explore the capabilities of this new system, and compare differences between processing of Ga$_2$O$_3$ and GaN on the same tool. Triethylgallium ([C$_2$H$_5$]$_3$Ga; TEG) and Ar/O$_2$ or Ar/N$_2$/H$_2$ plasmas are used to deposit Ga$_2$O$_3$ and GaN (T_{dep} = 200 °C), respectively. The Ga$_2$O$_3$ process has a short cycle time of 2 seconds, a growth-per-cycle (GPC) of 0.73 Å/cycle, and 3.8 % thickness non-uniformity on an 8 inch wafer. The GaN process has a cycle time of 6 seconds, a GPC of 0.33 Å/cycle, and a 15.6 % thickness non-uniformity on an 8 inch wafer. The films are close to stoichiometric, with carbon impurities <1 at. %, which confirms the deposition of high-quality films. The oxygen content in GaN is quite low at around 4 at. %. The material properties of GaN and Ga$_2$O$_3$ can be tuned using deposition temperature and rf substrate biasing. A higher deposition temperature leads to a higher density for GaN, while for Ga$_2$O$_3$ density does not change significantly for deposition temperatures between 100-200 °C. Furthermore, rf substrate biasing with DC bias voltages between 0 and -70 V affected both GPC and refractive index of GaN, which show the importance of precise ion energy control. This research has allowed for insights in the behaviour of this new ALD system, and shows that high-quality Ga$_2$O$_3$ and GaN films with short cycle times and controllable properties can be obtained.

References

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11:00am **AF2-TuM-13 Y$_x$C Thin Films Prepared by Plasma Enhanced Atomic Layer Deposition as a Diffusion Barrier and Glue Layer for Cu & Ru Interconnects**, *Minjeong Kweon*, C. Park, S. Kim, S. Kim, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Transition metal carbides (TMC) and nitrides (TMN) are widely used materials in industrial applications due to their exceptional hardness, high melting temperatures, and chemical stability [1]. In particular, transition metal carbides are stable at high temperatures with a higher phase transition temperature than other nitrides and oxides. Additionally, they possess excellent resistances to the oxidation and corrosion, making them valuable in various technological applications, including mechanical structures, the chemical industry, and nuclear power [2]. However, researches regarding both the processes of yttrium carbide (YC$_x$) thin film, one of the transition metal carbides, and their properties are still in the very early stages and pioneering studies exploring the deposition possibility of YC$_x$ thin film and its potential applications based on the characteristics of the deposited YC$_x$ thin film are necessary. In this study, YC$_x$ films were deposited by plasma enhanced atomic layer deposition (PEALD) (IOV dX1 PEALD reactor, ISAC Research, Korea) using a new Y metalorganic precursor and H$_2$ plasma as the reactant, at the deposition temperature ranged from 150 to 350 °C. With an increase in precursor pulse time and reactant pulse time, self-limited film growth, which is the typical characteristics of ideal ALD, was observed. Moreover, under the optimal pulsing conditions, a clear linear dependence of film growth on the number of ALD cycles was evident. The saturated growth per cycle (GPC) was approximately 1.3 Å/cycle. The

ALD–YC$_x$ films with the formation of nanocrystalline structures and a rhombohedral Y$_2$C phase were confirmed by XRD and XPS, with optimized deposition condition at 250 °C. STEM-EDS analysis showed that the composition was YC$_x$ (C/Y = 0.47). Additionally, experiments on the thermal stability of YC$_x$ films at high temperatures were conducted alongside XRD analysis. The step coverage of the film deposited at 250 °C was approximately 85%on the trench structures (bottom width of 120nm and aspect ratio of approximately 4.3). Finally, the PEALD-YC$_x$ deposited under optimized conditions is applied as a diffusion barrier for the Cu & Ru interconnects. The detailed results will be presented in the conference.

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11:15am **AF2-TuM-14 Plasma Enhanced Atomic Layer Deposition of Boron Nitride**, *Marc Reynaud,* University of Texas at Austin; *J. Zhao, J. Carroll, G. Blankemeyer, P. Ventzek,* Tokyo Electron America, Inc.; *J. Warner, J. Ekerdt,* University of Texas at Austin

The International Roadmap for Devices and Systems has identified challenges with continued device scaling and for future device architectures. With respect to interconnect technology requirements for logic devices, the challenges include "the introduction of new materials that meet the wire connectivity requirements, reduce dielectric permittivity and meet reliability requirements. The interlayer dielectric constant is projected to range from 3.2 to 2.2 for inorganic materials. Reaching these dielectric constants poses significant challenges. Conventional silicon dioxide based (SiCOH-based) dielectrics cannot reach these levels without introducing porosity that compromises the reliability of the film. Thin dielectric layers will be needed to serve as liners and etch stop layers along with the interlayer dielectric. Boron nitride (BN)-based thin films are promising materials for these applications as they possess attractive chemical, mechanical and electrical properties for the low-k environment integrated with Cu/Ru and Mo. Indeed reports have shown amorphous BN (a-BN) films with dielectric constants less than 3.0.

Here, we use PEALD to deposit boron nitride on Si(001) native oxide by alternating a thermal exposure of borazine (triazatriborinane), a single source precursor, at 25 and 100 °C, and a nitrogen-based plasma step. An experimental capacitively coupled radio frequency plasma source is used to understand how different plasmas, including ammonia, hydrogen, nitrogen, and pure argon, different frequencies, and plasma power impact the nature of chemisorption, film growth and film properties. Films are characterized using *in situ* X-ray photoelectron spectroscopy and *ex situ* using Raman spectroscopy, transmission electron microscopy and time of flight secondary ion mass spectroscopy.

ALD is realized at 25 °C using 300 mTorr exposures of borazine and converting adsorbed borazine into a-BN using a N$_2$/Ar plasma operating 100 MHz and 400 W power. Lower exposure pressures at the same Torr-s exposure result in undersaturation of the adsorbed layer and lower growth per cycle. Films are slightly N-rich and essentially carbon-free (0-2% carbon) with B:N compositions averaging B$_{0.46}$N$_{0.54}$.SiO$_2$/(Si001) pretreatment with a H$_2$/Ar plasma is required to create reactive sites for film nucleation on the native oxide. This talk will address the role of different plasma conditions on borazine adsorption and transformation into a-BN.

11:30am **AF2-TuM-15 Time-Resolved Study of OH Radicals During PEALD of Al$_2$O$_3$ by Advanced Laser Spectroscopy**, *Antoine Salden,* TU / Eindhoven, Netherlands; *M. Ceppelli, L. Martini,* University of Trento, Italy; *R. Engeln, H. Knoops, E. Kessels,* TU / Eindhoven, Netherlands

Radicals play an important role in PE-ALD due to their highly reactive nature, meaning that understanding their role in reaction mechanisms is crucial for subsequent process optimization. However, their interaction with the surface can be challenging to investigate due to their short lifetimes, given their reactive nature. While excited states can be readily detected by optical emission spectroscopy (OES), the radicals in the ground state — generally the bulk of radicals — are invisible to this technique. Furthermore, OES provides line-of-sight integrated measurements that make it arduous to decouple processes in the surface–environment from those in the plasma bulk.

To overcome aforementioned challenges, this study implements in situ active laser spectroscopy, in the form of laser induced fluorescence (LIF), to investigate the ground state of the OH radical during PE-ALD of Al$_2$O$_3$ using

$Al(CH_3)_3$ and O_2 plasma. By resonantly exciting ground state OH with a laser, the observed induced fluorescence from the $A^2\Sigma^+, v=0,1$ manifold is a measure of the ground state density. Owing to the high spatiotemporal resolution of the technique, we were able to measure the time-resolved, relative density of the ground state at different distances from the substrate surface, during the plasma step of the process. At the start of the plasma step, we observe a brief high density of OH in the plasma, which is caused by surface reaction products diffusing away from the surface. Close to the surface, however, in the plasma (pre)sheath, OH formation by electron impact is inhibited. Not only does this cause a decrease in density, it also changes the evolution in time of the density: OH close to the surface appears to originate from diffusion from the plasma. These trends are strikingly more intricate than the evolution that is observed by OES for characteristic emissions associated with surface reaction products — such as OH and CO from methyl-group combustion — as those signals are dominated by contributions from the plasma bulk. While different, the results between LIF and OES appear compatible with each other when accounting for diffusive transport. All in all, these results demonstrate the deeper insights gained from well-localized diagnostics, capable of probing the radical ground state with high time resolution, to further investigate the environment at the plasma–surface boundary during PE-ALD.

11:45am AF2-TuM-16 Engineering of VO_x Properties Through Control of Plasma Characteristics During Plasma-Enhanced Atomic Layer Deposition, *Peter Litwin,* U.S. Naval Research Laboratory; *M. Currie, N. Nepal, M. Sales, D. Boris, S. Walton, V. Wheeler,* US Naval Research Laboratory

Crystalline VO_2 (c-VO_2) undergoes a phase transformation between two crystalline states at ≈ 68 °C, which is accompanied by a metal-to-insulator transition (MIT). Below the critical transition temperature (T_c), c-VO_2 exists in the monoclinic crystal structure and is a semiconductor with a band gap of ~0.7 eV that is transparent to infrared light. Above the transition temperature c-VO_2 exists in a tetragonal crystal structure and behaves as a metal that is reflective to infrared light. The MIT in c-VO_2 is of interest for numerous applications such as passive thermal regulation (e.g. energy efficient windows), thermal sensors, and passive radio frequency components.

VO_2 films deposited by traditional (thermal) atomic layer deposition (ALD) processes are amorphous (a-VO_2) and thus do not exhibit a MIT. While the a-VO_2 films can be crystallized by a post-deposition annealing step, this limits the application space of ALD VO_2 due to thermal budget constraints. Plasma-enhanced ALD (PEALD) has been shown as a route to deposit crystalline materials by offering increased kinetics without the use of high substrate temperatures. This is made possible by the simultaneous delivery of a flux of both energetic and reactive plasma species to the growth surface. However, the enhanced reactivity of oxidizing-plasma sources poses challenges not present in thermal ALD processes. For example, control of the V oxidation state in thermal ALD is often dictated by the oxidation state of the V in the metal-organic precursor used during growth. For that reason, a V^{4+} oxidation state precursor is commonly used to promote the deposition of VO_2 in thermal ALD. Conversely, the strong oxidation characteristics of oxidizing-plasma sources used in PEALD typically result in the growth of V_2O_5, i.e., V^{5+}, regardless of the metal-organic precursor used.

Here we present studies investigating the role of O_2-plasma characteristics on the stoichiometry and crystallinity of VO_x thin films deposited by PEALD. A focal point of these studies is correlating plasma properties, including plasma power, Ar/O_2 ratio, system pressure, and total gas flow during the plasma step with the control of the V^{4+}/V^{5+} ratio and crystallinity, as probed by x-ray photoelectron spectroscopy and Raman spectroscopy. Initial results, based on a typical Ar/O_2 plasma used for ALD Al_2O_3 films, show a mix of the V^{4+} and V^{5+} oxidation states with evidence for the crystalline forms of each. Further optimization will be discussed and, where applicable, hysteretic characteristics of the MIT in PEALD VO_2 films are benchmarked against traditional annealed, thermal ALD films using optical transmittance.

Atomic Layer Etching
Room Hall 3F - Session ALE1-TuM

ALE Applications and Methodologies

Moderators: Hannah Margavio, North Carolina State University, **Fred Roozeboom**, University of Twente and Carbyon B.V., The Netherlands

8:00am ALE1-TuM-1 Current Status of ALE in Semiconductor Processes, *K. Bai, Sang Hyun Lee,* Samsung Electronics Co., Republic of Korea **INVITED**
ALE process has been studied and used in the semiconductor processing for years.

There are a few benefits with the ALE, not only higher selectivity but also fine etch amount control or less loading.

In this presentation, we review the status of the ALE in the Fab for semiconductor manufacturing. What kinds of ALE and how much has it been adapted in the fab till now.

Considering the merits of the ALE, it has not been adapted widely. We will review the issues of the process in the line and what is necessary for more wide spread of the ALE.

8:30am ALE1-TuM-3 ALE Preparation of Diamond Surfaces for Materials and Device Applications, *Jeffrey Daulton, M. Geis, M. Polking,* MIT Lincoln Laboratory
The expected high performance of ultrawide-bandgap semiconductors, resulting from the superior critical field, mobility, and thermal conductivity, has created substantial interest for their use electronics. Polishing of such substrates, however, has generally proven problematic, as the high bond energy that results in their wide bandgap also makes these materials relatively chemically-inert, limiting the effectiveness of CMP. Diamond, in particular, tends to form significant defects during the polishing process. As a consequence of the diamond sp^3 phase being metastable under standard conditions, these defects generally exhibit graphitic sp^2 bond character, making them readily etched in hydrogen plasmas. This results in even short exposures to hydrogen plasmas forming deep, crystallographically-etched pits in the polished surface. This has the effect of significantly limiting the quality of epitaxial growth on such surfaces, as diamond CVD growth inherently relies on initiation of the growth process with a hydrogen plasma. Such highlighting of defects also has negative implications for the mobility of diamond surface FETs, where the such a hydrogen plasma exposure is used to terminate the diamond surface and form a high-density 2-dimensional hole gas (2DHG) channel on the surface.

Smoothing by ALE has been demonstrated across a wide range of materials, suggesting the possibility for its use in pre-epitaxy surface preparation, provided near-surface plasma damage can be reduced sufficiently. Here, we use a Cl_2/Ar ALE cycle to prepare very smooth (Ra = 0.058 nm) diamond surfaces. Because of the tendency of damaged diamond to exhibit graphitic sp^2 bond hybridization, we use Raman spectroscopy, which is capable of differentiating between the diamond sp^3 peak and the graphitic sp^2 phase. This allows for observation of any reduction of near-surface damage with ICP etching or with ALE. Raman spectroscopy shows a clear reduction in sp^2 bonding with ALE from the ICP-etched surface, suggesting that this process removes the lattice damage induced by the ICP etching process. The remaining shallow, uniform sp^2 surface layer can then be easily removed during initiation of CVD growth to yield a high-quality growth interface.

8:45am ALE1-TuM-4 Comparison of Different PEALE Modes on AlGaN/GaN Heterostructures, *C. Miersch, Sarah Seidel,* Fraunhofer Institute for Integrated Systems and Device Technology IISB, Germany; *A. Schmid, J. Heitmann,* Department of Applied Physics, Technical University of Freiberg, Germany; *F. Beyer,* Fraunhofer Institute for Integrated Systems and Device Technology IISB, Germany
Nitrogen based group III-V compound semiconductors have become an integral part of consumer electronics and are essential for high-power and high-frequency applications. The Baliga's figure shows especially for GaN and AlN offer theoretically a high break down voltage (GaN: 5 MV/cm [1] and AlN: 15 MV/cm [2]) at low specific on-resistance [3,4]. Transistors based upon nitride semiconductors are high electron mobility transistors (HEMTs)

and it can be realized by a heterojunction of an AlGaN barrier to a GaN buffer layer is forming two-dimensional electron gas (2DEG) [5,6], due to spontaneous and piezoelectric polarization. This normally-on transistors are desirable normally-off, which increases the safety for power-switching applications and suits to the established MOSFET circuit design. One way to shift the threshold voltage V_{th} in positive direction is to bring the gate contact closer to the channel by a precious and damage free recess etch of the AlGaN barrier (Fig. 1) [7]. This requires increasing demands on the manufacturing processes like dry etching to achieve smaller and high controllable etching rates, low damage, and minimized surface roughness. For this challenge atomic layer etching (ALE) is ideal. A conventional ALE approach on a AlGaN/GaN heterostructure could be described as followed. In the first step, the so-called modification step, the surface is modified by chlorine etching chemistry, producing a thin layer, ideally on an atomic scale, of volatile $GaCl_x$ and $AlCl_x$ products. In the second step, the so-called removal step, this thin layer can be easier removed then the unmodified surface below, by a physical impact of accelerated low energy Argon-ions. Typically purging in between the steps is applied, which increases the cycle time and affects the processing costs. An optimization of the cycle times and the implementation of other ALE methods can be beneficial.

For the experiments, a plasma enhanced ALE is used for etching. In this study, we develop an ALE recipe for the $Al_{25}Ga_{75}N$ barrier layer and optimized it in respect to the cycle times and the plasma damage. Furthermore, we compare different ALE methods: with purging in between the steps, purge-free [7], continuous plasma and a bias-pulsed [8] option. The evaluation of the developed processes will be performed by morphological and electrical characterization (gate recessed HEMTs). The induced damage will be investigated by structural and defect spectroscopical analysis.

9:00am ALE1-TuM-5 Quasi-ALE Process for GaN: High Etching Rate Without Compromising the Surface Roughness, *P. Mouriño-Miñambres, R. Resta-López, F. Martín-Romero,* **Miguel Sinusia Lozano***, V. Gómez,* Nanophotonics Technology Center - Universitat Politècnica de València, Spain

The atomic layer etching (ALE) process allows, theoretically, the selective atomic layer etching of the selected compound. In this work a Cl-based ALE process is developed to etch Ga-polar GaN (0001). Several parameters of the etching process are evaluated for assessing their influence on the ALE process namely, the ratio of the cycle devoted either to chlorination or Ar-sputtering and the applied RF power. The developed etching process, carried out at 5 mTorr, provides EPC values as high as 4 nm per cycle. Furthermore, because of the low-energy Ar plasma sputtering step, the etching process does not degrade the surface properties as reflected by the atomic force microscopy (AFM) and photoluminescence (PL) measurements without degrading the surface roughness [1]. Similar to other ALE processes reported in the literature, the smoothness of the surface is improved [2,3]. However, in comparison the EPC cycles in this work are larger-without any purge step within the cycle- thus reducing the time needed when the ALE process is applied during the nanofabrication process.

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1. Mannequin, C.; Vallée, C.; Akimoto, K.; Chevolleau, T.; Durand, C.; Dussarrat, C.; Teramoto, T.; Gheeraert, E.; Mariette, H. Comparative Study of Two Atomic Layer Etching Processes for GaN. *Journal of Vacuum Science & Technology A* **2020**, *38*, 032602, doi:10.1116/1.5134130.
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9:15am ALE1-TuM-6 A New Challenge for Developing Novel Atomic Layer Etching: Applying the Leidenfrost Effect to Obtain Floating Nanomist-Assisted Vapor Etching*, Thi-Thuy-Nga Nguyen,* Nagoya University, Japan*; Y. Yamaguchi, K. Shinoda,* Hitachi, Ltd., Japan*; K. Sun,* Nagoya University, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective etching of three-dimensional nanostructures in semiconductor devices requires a high-performance etching technology. In our previous study, we developed a wet-dry etching or wet-like plasma etching that combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability) [1]. By using a high-density vapor plasma (wet-like plasma) at medium pressure, high-density reactive radicals are generated, significantly increasing the chemical reaction rate to the sample surface. This paves a new path for our development of the new dry atomic layer etching methods, named wet-like atomic layer etching (ALE).

Here we have proposed a new wet-like ALE method, named floating nanomist-assisted vapor ALE at relatively low temperature, that is aiming to minimize the damage from sputter effect in plasma ALE, high temperature treatment in thermal ALE during volatilization, and nanostructure damage in wet ALE. The phase with intermediate properties between mist liquid phase and vapor phase, named mist-vapor phase or nanomist phase that can maintain the wet properties of liquid phase at the minimal size less than 100 nm is proposed here for nanodevice applications. At the Leidenfrost point, the nanomist floats on its own stable vapor cushion film over the whole sample surface [2]. By using the Leidenfrost effect, the sample surface can be modified and/or etched by the floating nanomist-assisted vapor, this is an optimal condition to obtain an ultra-thin liquid-like layer in the shortest time. In the first step of cyclic process, the nanomist A is introduced and approaches the sample surface to form the floating nanomist A. Under the floating nanomist A, a stable vapor film A exists and reacts with the sample surface to form a modified layer. In the second step, the modified layer is removed by dissolving it in the highly volatile nanomist B flow, resulting in a clean surface and a controllable cyclic process.

An example of trying to apply the Leidenfrost effect to obtain floating nanomist-assisted vapor etching is demonstrated here for TiAlC film by using the H_2O_2 based mixtures at medium pressure. The nanomists of these liquid mixtures were generated by an originally developed atomizer that was controlled at room temperature. The highest etch rate of TiAlC film was obtained at the temperature of 175 °C that is considered as the Leidenfrost point of the nanomist produced from the aqueous liquid mixture, in which the TiAlC surface is supposed to be etched by the floating nanomist-assisted vapor.

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9:30am ALE1-TuM-7 Electron-Enhanced Etching of Molybdenum Using Sequential O_2 and HCl Reactive Background Gases to Form Volatile Molybdenum Oxychlorides*, Michael Collings, S. George,* University of Colorado, Boulder

Molybdenum (Mo) is important for future back-end interconnects resulting from its favorable resistivity scaling as metal lines continue to shrink. Precision etching techniques are needed to fabricate these interconnects and clean the metal contacts. In this study, Mo etching was achieved utilizing O_2 and HCl reactive background gases (RBGs) in conjunction with low energy primary electrons at ~100 eV to create volatile Mo oxychloride products. The electrons can dissociate O_2 and HCl to generate ions or radicals. The electrons can also desorb surface species by electron stimulated desorption (ESD). In addition, the primary electrons at ~100 eV can form secondary electrons at lower energies. The primary electrons were obtained from a hollow cathode plasma electron source (HC-PES). The HC-PES is a chemically robust electron source that can deliver currents >200 mA over an area >10 cm^2.

Electron-enhanced etching was demonstrated on Mo films using sequential O_2 and HCl RBGs. Oxygen was dissociated by the electron beam and oxidized the Mo surface to form MoO_x. The Mo oxidization was dependent on the voltage potential on the substrate. In situ spectroscopic ellipsometry (SE) measurements of the MoO_x film thickness showed that Mo oxidation with a +20 V stage voltage was >7X faster compared with oxidation using a 0 V or -20 V stage voltage (Figure 1). We believe that the positive stage voltage can activate a new process mechanism involving secondary electrons (Figure 2). The attachment of secondary electrons to O_2 produces O_2 dissociation. O_2 dissociation creates negative O^- ions that are then attracted to the positive stage voltage. This mechanism explains the greatly enhanced oxidation rates with positive stage voltage.

Subsequently, the HCl RBG was dissociated by the electron beam to form chlorine species. The reaction of chlorine species with the MoO_x surface produces volatile MoO_xCl_y compounds. In situ SE measurements of the MoO_x film thickness monitored the etching of MoO_x by HCl RBG (Figure 3). The MoO_x etching was also dependent on the stage voltage. Low etching rates were observed at stage voltages ≤ +20V. Greatly enhanced etch rates were observed at stage voltages ≥ +30V. This enhancement is also attributed to secondary electrons that create Cl^- from the HCl RBG after dissociative electron attachment. Secondary electron emission from samples followed by electron attachment to form negative ions provides a

new class of reactive species for etching. Positive stage voltages can be used to pull the negative ions to the substrate to enhance the etch rates.

9:45am ALE1-TuM-8 Impact of Activation Strategies for Sio₂ Atomic Layer Etching Applied to Contact Patterning, *Antoine Ronco, F. Boulard, S. Lecré,* Univ. Grenoble Alpes, CEA, Leti, France*; N. Possème,* ST Microelectronics, France

The etching of SiO_2 for contact etching is classically carried out using continuous reactive ion etching (RIE). However, the development of novel architectures for advanced devices and applications often uncover new problematics. This motivates the refinement of etching techniques and processes, in order to etch high aspect ratio (HAR) features while maintaining very high values of selectivity to the underlying layer [1]. For this reason, Atomic Layer Etching (ALE) is receiving attention as it promises to enable a higher control of the process than RIE. In the case of SiO_2, to maintain throughput and etch HAR patterns, the contact etching process is carried out in a Capacitively Coupled Plasma (CCP) reactor. In these conditions, reaching ideal ALE is challenging for two reasons: the non-self-limited nature of the modification step, and the difficulty of obtaining an ideal activation step [2]. This way, developing processes that are free from variability such as aspect ratio dependent etching (ARDE) or intra-wafer non-uniformity is needed.

This work presents developments of Quasi ALE processes of SiO_2 and focuses on different strategies for the optimization of the activation step in order to increase the robustness of these processes.

Blanket and patterned samples are studied. Blanket samples consists of SiO_2 on Si wafers. Patterned samples consists of SiO_2 on SiN on Si wafers. These experiments are performed in a 300 mm FLEX FL CCP reactor from Lam Research. The modification step is carried out with a C_4F_6 / Ar plasma using the high frequency power generator. The activation step consists of an Ar plasma using the high and low frequency generators. The reactor is cleaned using an O_2 plasma before and after etching each wafer. Etch rates of SiO_2 and SiN are determined by ellipsometry and cross-section SEM.

The sputtering threshold of SiO_2 in low-pressure Ar plasma is investigated depending on the RF power used on the low and high frequency power generators. Conditions of ideal ALE activation in CCP and the implications on throughput are reported.

To limit ARDE and etch stop, alternative activation strategies are investigated through the addition of O_2 to the Ar activation plasma. The impact on pattern shape and SiO_2:SiN selectivity at the bottom of the contact is studied.

Finally, the implementation of a three-step cycle, with a deposition, activation and cleaning step, is investigated. The use of the cleaning step during each cycle or punctually after a certain amount of cycles is discussed, along with the development of said cleaning step.

[1] T. Bédécarrats et al., IEEE (IEDM), (2021).

[2] K. J. Kanarik et al., JVSTA **33**, no 2, 020802, 2015

Atomic Layer Etching
Room Hall 3F - Session ALE2-TuM

Thermal Gas-phase ALE

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Jean-François de Marneffe**, IMEC

10:45am ALE2-TuM-12 Thermal Etching of Metals and Metallic Materials for Gate-All-Around Devices, *Dimitri Kioussis, S. Karumuri, M. Uddin, S. Barnhill, Y. Huang, B. Erickson,* Intel Corporation **INVITED**
Isotropic Vapor Etch and Atomic Layer Etching (ALE) with extreme high selectivity have become essential technologies to continue Moore's law cadence for fabrication of next generation logic transistors beyond 2nm node. This talk reviews the status of Vapor Etch and ALE processes at Intel for etching various materials such as metals, metal nitrides, and metal oxides used across various sections of the process flow. The talk will outline basic thermodynamic principles and reaction kinetics as they apply to these reactions. Will discuss why in the nonsaturation mode etch anisotropies may occur that can lead to unwanted performance variations in high aspect ratio devices due to topological constraints imposed on the delivery of reactants and removal of reactant by-products. While ALE involves sequential modification of the etch surface followed by ligand exchange to etch the material, thermal pseudo-ALE (Tp-ALE) uses thermal activation, instead of surface modification. Thereby, ligand exchange reacts with

metal/metallic surfaces with or without surface modification. These two unique approaches offer atomic layer precision in removing metals/metallic films selective to other materials in the stack. This talk will briefly demonstrate the capability of ALE, Tp-ALE as well as combination approach in etch back, recess, and complete removal applications.

11:15am ALE2-TuM-14 Low Temperature, Conversion-Free Thermal Atomic Layer Etching of Zinc Oxide using Hydrofluoric Acid and Trimethylgallium, *Taewook Nam, D. Zywotko, J. Partridge, S. George,* University of Colorado Boulder
Thermal atomic layer etching (ALE) processes have been developed based on various etching mechanisms. For example, metal oxides such as Al_2O_3, HfO_2, and ZrO_2 are etched based on "fluorination–ligand exchange" reactions. ALE studies have also shown that materials can be converted to a different material by reaction with the ALE precursors. The "conversion" based etching mechanism has been confirmed for ZnO ALE using hydrofluoric acid (HF) and trimethylaluminum (TMA). This study introduces a conversion-free thermal ZnO ALE using HF and trimethylgallium (TMG). ZnO thermal ALE using HF and TMG was studied using a variety of techniques including quartz crystal microbalance (QCM) and quadruple mass spectrometry (QMS). ZnO films were first deposited using atomic layer deposition (ALD) using diethylzinc (DEZ) and water (H_2O) at 100 °C. QCM measurements during ZnO ALE then observed digital mass gains during HF exposures and pronounced mass losses during TMG exposures. Under saturation conditions, the etch rates were 0.24, 0.52, 0.97, 1.35, 1.92, and 3.82 Å/cycle at 30, 60, 100, 150, 200, and 300 °C, respectively. One notable difference between ZnO ALE using HF/TMA or HF/TMG is that the etching can be achieved at 30 °C using HF/TMG, whereas ZnO ALE using HF/TMA requires temperatures ≥ 240 °C. To understand the temperature differences between the two chemistries, TMA and TMG were individually exposed to fresh ZnO ALD films. The mass after TMA exposure showed a pronounced decrease because of the conversion reaction. The TMA exposure converts ZnO to Al_2O_3. HF can then adsorb on the fluorinated Al_2O_3 surface. Subsequently, this HF can react with TMA to produce AlF_3 ALD at temperature < 240 °C. In contrast, the mass increased after TMG exposure on fresh ZnO ALD films because of TMG adsorption on the ZnO surface. HF then fluorinates ZnO to ZnF_2 and HF does not strongly adsorb on the ZnF_2 surface. Consequently, TMG does not react with HF to produce GaF_3 ALD. Because GaF_3 ALD does not compete with ZnO ALE, ZnO ALE can be performed at extremely low temperatures down to 30°C. QMS experiments were also performed to identify etch products during ZnO ALE using HF and TMG. The QMS experiments support the "fluorination-ligand exchange" reactions without conversion during ZnO ALE using HF/TMG.

11:30am ALE2-TuM-15 Thermal Atomic Layer Etching of the Indium Gallium Zinc Oxide (IGZO) Family by Fluorination and Ligand-Substitution Hydrogen-Transfer Reactions, *Troy Colleran, J. Partridge, A. Abdulagatov, S. George,* University of Colorado at Boulder
Indium Gallium Zinc Oxide (IGZO) and its component metal oxides are important oxide semiconductors. Etching these metal oxides will be needed to fabricate thin channels for transistors. The thermal ALE of In_2O_3, Ga_2O_3, ZnO, and IGZO was achieved using sequential fluorination and ligand-substitution hydrogen-transfer (LSHT) reactions at 200°C. The two-step etching process was performed by first fluorinating the metal oxide using HF. Following fluorination, volatile release of the metal fluoride was accomplished using acetylacetone (Hacac). LSHT with Hacac leads to volatilization of the metals as stable, metal acetylacetonate compounds ($M(acac)_x$; M = In, Ga, Zn). During the LSHT reaction, acac from Hacac substitutes for fluorine in the metal fluoride. Hydrogen from Hacac also transfers to the metal fluoride to form HF. Etching of IGZO films was measured by *in situ* spectroscopic ellipsometry studies. IGZO etch rates of 0.3, 0.4 and 0.6 Å/cycle were measured at 200, 230 and 250°C, respectively, on IGZO thin films. Quadrupole mass spectrometry (QMS) studies also measured the etching of In_2O_3, Ga_2O_3 and ZnO powders at 200°C. In_2O_3 and Ga_2O_3 ALE were confirmed by the evolution of $In(acac)_3$ and $Ga(acac)_3$, as well as HF, during Hacac exposures after fluorination of the respective metal oxide. ZnO was found to be spontaneously etched by Hacac as evidenced by the continuous evolution of $Zn(acac)_2$ and H_2O during Hacac exposure despite no previous fluorination. Time-dependent studies of the etch products were also performed using QMS. The evolution of $M(acac)_x$ and HF during Hacac exposures on a previously fluorinated metal oxide was consistent with the proposed etch mechanism. The decay in $M(acac)_x$ signal intensity during Hacac exposures was evidence of self-limiting LSHT reactions. The spontaneous etching of ZnO using Hacac exposures did not prevent the thermal ALE of IGZO films.

11:45am ALE2-TuM-16 Designing an ALE Process and Uncovering the Etching Mechanism for a 2D van Der Waals Material: Ternary Transition Metal Chalcogenide CrPS$_4$, *Marissa Pina*, M. Whalen, J. Xiao, A. Teplyakov, University of Delaware

CrPS$_4$ is a 2D van der Waals material in the ternary transition metal chalcogenide (TTMC) class of compounds. CrPS$_4$ is a semiconductor with A-type antiferromagnetic ordering, so thin flakes a few layers thick can display ferromagnetic or antiferromagnetic behavior depending on whether there is an odd or even number of layers.

In order to understand the magnetism down to the monolayer limit and their dynamic excitations in magnons and excitons, and make devices based on 2D magnetic materials viable for industry, 2D materials with well-controlled layer structures have to be produced. The existing methods for controlling CrPS$_4$ thickness, such as mechanical and liquid exfoliation, are either not well controlled or introduce damage to the crystal structure. In this study, we will show that thermal atomic layer etching (ALE) can be used to controllably etch the 2D crystals of this material without contaminating them. Ultimately, using ALE to manipulate the thicknesses of these flakes will allow for controlling their magnetic and dynamic optical properties.

CrPS$_4$ flakes were exfoliated onto a gold film from a single crystal via mechanical exfoliation. Thermal ALE cycles were performed in an ultra-high vacuum chamber. Each cycle consisted of a chlorine dose at elevated temperature using a solid-state electrochemical chlorine source, followed by an acetylacetone dose at elevated temperature. Atomic force microscopy was used to determine an average etching rate of 0.10 ± 0.07 nm/cycle. Although the etching rate appeared to depend on the thickness of the flakes, this average removal rate was recorded for 75 different points for flakes ranging from several nanometers to 90 nm in thickness. ALE also removed the island defects caused by exfoliation from the top of the flakes. XPS and ToF-SIMS were used to follow chemical changes in the material and to interrogate the distribution of etchant components within the flakes. The formation of chemical species containing acetylacetonate ligands was confirmed for all the components (Cr, P, S) of this TTMC, and the chlorination was followed in ToF-SIMS depth-profiling experiments. The ALE process that resulted in controlled material removal did not result in measurable surface contamination. Importantly, the etching of CrPS$_4$ is highly temperature-dependent, as lowering the process temperature by even 30 °C does not result in noticeable etching.

ALD for Manufacturing
Room Hall 3E - Session AM-TuM

Equipment Design, Precursor Delivery, and Spatial/R2R/Fast ALD
Moderators: Doug Agnew, LAM Research, **Ganesh Sundaram**, Veeco-CNT

8:00am AM-TuM-1 Development of a Modular Manufacturing Equipment Architecture for Application Tailored Process Options, *Jacques Kools*, Encapsulix SAS, France **INVITED**
The phenomenon of degradation of products by their sensitivity to undesired chemical reaction with the surrounding environment («aging»,«corrosion»,"tarnishing" etc.) is often a major factor limiting the useful lifetime of these products. Ultrabarriers mitigate these chemical reactions as they provide a diffusion barrier for the external reactant, which can vary from atmospheric water vapor and oxygen (e.g. for organic semiconductors in OLED and perovskite PV applications), to salt water in automotive or marine applications bodily fluids (which contain salt), ...etc. Among the different methods used for ultrabarrier deposition, ALD has been found to provide the best performance, due to the low defect density and 3D conformality of the coatings. Furthermore, the unique ability of the ALD method to manipulate the film material at the atomic level provides an exciting avenue to develop application-optimized barrier structures. Thereby it is interesting to combine the primary functionality (i.e. barrier suppressing an undesired chemical reaction) with secondary functionalities (antimicrobial, self cleaning, decorative,...). As a result, advanced ultrabarrier processes comprise a variety of Atomic Layer Processing (ALP) steps, such as preclean/etch/nanostructuring,, and multilayer/nanolaminate deposition plasma stress release/densification using a variety of metal precursors and oxidizing co-reactants. The combination of this cornucopia of process and associated equipment options, and the large spectrum of application requirements provides both an opportunity and a challenge in the transition from lab to fab: • For the chemical reactants supplier, novel (esp. more selective and sustainable)

chemical production flowcharts will meet future industrial and legal requirements. • For the device maker, it now becomes possible to tailor an optimized ultrabarrier nanostructure to the specific requirements of their application, thus enabling industrial feasibility and creating possible IP in novel processing. • For the equipment supplier, the challenge is to minimize both non-recurring engineering and unnecessary complexity to ensure competitive equipment cost of ownership and reliability. In this talk, we will discuss how Encapsulix addresses these challenges through the development of a modular equipment system, which allows for easy equipment configuration, both prior to delivery and for future upgrades as needed to support a product roadmap. We will review some general architecture aspects , and discuss a number of application examples (e.g. IT, energy and medical)

8:30am AM-TuM-3 Optimizing Precursor Utilization for Spatial ALD in High Surface Area Substrates, *J. van Himste*, SparkNano B.V., Netherlands; *Paul Poodt*, SparkNano B.V. and Eindhoven University of Technology, Netherlands
Atomic Layer Deposition is well known for its ability to deposit thin films inside high surface area and porous substrates, with precise control of the step coverage and thickness. For these reasons, the use of ALD for new applications is being developed, where this precise control of step coverage and thickness is essential. Examples include the deposition of precious metal electrocatalysts on high surface area catalyst supports for water electrolysis and fuel cells, and the deposition of very thin passivation layers inside Li-ion battery anodes and cathodes. A challenge is that these applications require a high deposition rate and high throughput way of doing ALD, often in a roll-to-roll mode, for which Spatial ALD can be the solution.

Using the precursor dose to control he step coverage and deposition rate inside porous substrates has been widely reported on in literature. The simplest way to increase the deposition rate is by increasing the partial pressure of the precursor. However, next to practical limits in precursor volatility, using high precursor partial pressures can lead to very low precursor utilization rates. With precursor prices ranging from a few $/gram to 100's of $/gram, low precursor efficiencies are not feasible for most applications.

Here, we will show the results on modeling and experimental work on optimizing the precursor utilization efficiency during Spatial ALD on a variety of porous substrates. To objective is to minimize the precursor mass flow (e.g. in grams/hr) while ensuring a high enough precursor dose to realize the desired step coverage. By combining experiments and modeling on gas flows, precursor diffusion and surface reactions we can estimate optimized process conditions as a function of aspect ratio, surface area, required throughput, temperature and pressure. We will show that by carefully optimizing the precursor partial pressure and mass flow, precursor utilization efficiencies >90% are possible.

In cases where these high efficiencies are not attainable, or in case of very expensive precursors (e.g. containing precious metals), we have investigated the possibility to reclaim unreacted precursor for recycling. We will show results on precursor reclaim experiments, showing that reclaim efficiencies of up to 90% are feasible. By combining accurate process optimization and precursor reclaim, it is possible to perform ALD with extremely low precursor waste, which is an important enabler for high throughput and low cost Spatial ALD for a range of existing and new applications.

8:45am AM-TuM-4 Development and Scale-up of ALD onto Synthetic Graphite Powder in a Continuous Vibrating Reactor for Battery Applications, *B. Castro*, Forge Nano Inc; *A. Broerman, C. Gump, Arrelaine Dameron*, Forge Nano
As the demand for improved performance in battery material increases, development of large-scale, high-throughput ALD processes and equipment is necessary to meet production demands. Forge Nano has previously demonstrated ALD deposition onto natural and synthetic graphite over a range of scales (50 g – 50 kg) in both rotary bed and fluidized bed reactors. This process has now been successfully scaled-up to the highest throughput system (ton scale) with a continuous vibrating reactor (CVR). The CVR (and associated product Circe) is a spatial ALD system where the substrate powder travels down a porous deck, driven by vibration. Process gases flow at atmospheric pressure perpendicularly to the powder flow, up through the porous deck, and fluidize the moving powder bed and mixing the particles with the gases top to bottom in the process. The substrate travels through zones of the precursors and purge gases of an ALD cycle (Figure 1).

Reproducibility per batch and relative to successful graphite deposition criteria from smaller ALD batch systems was explored in a CVR system configured to perform 4 TMA/H_2O ALD cycles. Commercial synthetic graphite was coated at a rate of 33 kg/h, in 45-50 kg batches, at 180°C. Precursor flow was controlled based on the calculated stoichiometry required to achieve 100% titration of available surface sites, as determined in experiments performed in small scale fluidized bed reactors. Samples of coated product were taken from the reactor effluent every 10 minutes. Effluent samples of replicate runs were analyzed using ICP to determine the Al loading, and to characterize the reproducibility of the coating process. For all runs, the deposition of Al was deposited with an average of 84 ± 13 ppm Al (Figure 2).The initial samples for a given run were typically lower in deposition, likely due to the system approaching steady state in terms of substrate and precursor flow. Additional tests with 150% of the calculated stoichiometric TMA flow rate showed the deposition to be self-limiting. Finally, coated material was recycled through the CVR to demonstrate reproducibility that higher deposition levels and bed height and speed conditions were explored to achieve higher material processing rates. Coated materials were tested in coin cells as anode powders for lithium-ion batteries, with performance being compared to coated graphite prepared via more traditional deposition in fluidized bed reactors under vacuum conditions.

9:00am AM-TuM-5 Ultra High Speed Spatial PEALD Using a Novel Precursor Separation Method, *Eric Dickey,* Lotus Applied Technology

Spatial ALD has been shown to significantly improve deposition speed when compared with conventional temporal ALD, and spatial ALD reactors are now available from multiple equipment manufacturers for high-speed batch processing based on a rotating turntable configuration.For deposition of metal oxide films, most of these systems are based on a single metal precursor zone and a single oxidation zone, separated by differential flow and pumping.In this work, we characterize a plasma-based spatial ALD process in which the spatial "separation" of the ALD half reactions is achieved by using a different mechanism.Specifically, all of the gaseous material utilized for the oxidation step is exhausted into the larger overall volume of the reactor, which also contains the metal precursor vapor.Vapor phase interaction between the metal precursor and oxidant is prevented by the neutralization of the oxidation radicals on their path from the plasma to the overall volume of the reactor.This radical neutralization is achieved by enclosing the plasma electrode within a gas shroud having a high aspect ratio gas exhaust path into the chamber, allowing radical recombination in this exit path from the plasma.For some precursors that react with atomic oxygen, but not with ozone at the selected processing temperature, it is shown that merely by using this plasma gas exhaust configuration with molecular oxygen gas, effective separation is achieved.This is possible due to the rapid neutralization of atomic oxygen in the gas volume via recombination, given the relatively short mean free path at the pressure used for this process.For metal precursors that are reactive with ozone at the selected processing temperature, additional measures must be used to further enhance ozone depletion in the exhaust path.It is shown that by substituting carbon dioxide for oxygen used as the plasma gas, the amount of ozone exiting the shroud is reduced by orders of magnitude.For further reduction, an active catalyst is applied to the surface of the shroud in the gas exit path, which is shown to again reduce the amount of ozone exiting the shroud.Applying these principles, multiple plasma sources, including the radical neutralization feature, have been deployed in a rotating turntable spatial ALD prototype reactor, with a compact one-meter square footprint.This system demonstrates true PEALD processing of SiO_2 at coating speeds in excess of 25 angstroms per second.

9:15am AM-TuM-6 An Innovative 3D Solution for High Throughput Roll-to-Roll ALD, *Diederick Spee,* Kalpana Systems, Netherlands*; A. Ghazy,* Kalpana systems, Netherlands

ALD is currently the state-of-the-art thin film fabrication technology. Semiconductor industry relies on ALD in its manufacturing process [1]. However, the main drawback of the typical temporal ALD is the slow processing times. This has fuelled the creation of batch processing tools, and more importantly spatial ALD (S-ALD). In S-ALD the spatial separation between the precursor and the co-reactant replaces the time distinction of consecutive precursor pulsing, which results in saving processing times [2].

Roll-to-roll (R2R) Flexible substrates have become essential to next-generation applications including batteries, solar cells and OLEDs. It is also essential for packaging materials and barrier layers [3,4].Nevertheless, scaling up of roll-to-roll (R2R) S-ALD to a manufacturing level with high throughput has been challenging so-far.

The challenges entailed in making R2R S-ALD equipment compatible with high volume production environments are mostly related to throughput and up-time. To maximize both simultaneously, perfect precursor separation is necessary to avoid contamination. Particularly at high web speeds, i.e. high throughput can only be achieved with a small gap between deposition head and the substrate. This is challenging when using large, highly flexible substrates.

Kalpana Systems has developed equipment that combines an innovative web transport system with a moving deposition head (Figure S1), in such a way that the position of the substrate, relative to the deposition head, is controlled continuously and accurately.

In addition to providing compatibility with large scale production environments, our 3D machine configuration provides the possibility for deposition of complex layer stacks in one process and enables the efficient coating of porous and high aspect ratio substrates.

We will show our latest results on coatings for flexible PV, OLED and battery electrodes.

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9:30am AM-TuM-7 A Novel Technique for Pulsed Liquid Source Vapor Delivery in ALD and Short-Pulse CVD, *Kathleen Erickson, T. Sandbakken,* MSP - A Division of TSI

The short processing times necessary for ALD and short-pulse CVD pose a unique challenge to precursor vapor delivery. Bubblers or ampoules in conjunction with a downstream ALD valve can be a straightforward solution; however mass delivery accuracy, adjustability and stability are known issues, which can create thin film irregularity and wafer-to-wafer variability. Additionally, if precursors are thermally sensitive, there can be issues with the liquid decaying in the heated ampoule over time. Direct Liquid Injection (DLI) is a solution to ampoule/bubbler concentration stability and thermal decomposition issues. However, historically, DLI systems have suffered from long liquid flow stabilization times which typically require liquid or vapor divert; wasting expensive liquid precursors, reducing pump lifetimes and reducing throughput. This paper presents an alternative to these two conventional techniques for ALD and short-pulse CVD vapor delivery via a high-speed Liquid Flow Controller (LFC), and a new liquid source vaporizer; exploring the possibility of using DLI for ALD/CVD applications without the use of liquid/vapor divert.

The LFC contains a custom engineered high-precision liquid flow sensor with a scan interval of 11.5ms, enabling liquid flow measurement of sub-1s pulses. The vaporizer has the capacity to effectively vaporize up to 12g/min TEOS (or equivalent), while at the same time having minimal dead and internal volume. The LFC remotely controls a piezo valve on the vaporizer, to provide faster liquid/vapor response. During this study, the LFC/vaporizer combination was used in two ways; 'digital' in which the piezo valve was fully opened at the start of the pulse and then fully closed at the end of the pulse, and 'analog' where the LFC controlled the position of the piezo-valve via a liquid flow-rate feedback loop during the pulse. LFC measured flow rate was monitored by a high-speed data acquisition system, and downstream vapor pressure pulses were measured for pulse height, pulse width, consistency and timing offset. In 'digital' experiments, both a piezo driver and the 2950 LFC were used to fully open/close the piezo valve. The 'analog' experiment included exploring several PID techniques including a variety of voltage offsets, both static and dynamic.

This presentation will briefly detail the hardware and experimental setup used. 25ms, 50ms, 150ms and 500ms liquid/vapor pulse data will be presented. Repeatability, key control criteria, and advantages and disadvantages will be discussed.

9:45am AM-TuM-8 In-situ Spectroscopic Ellipsometry During Spatial ALD of Al₂O₃, ZnO, and SnO₂, *Melika Motaghian, M. van de Poll, S. Ratnasingham,* Eindhoven University of Technology, Netherlands*; H. de Vries,* SALD B.V., Netherlands*; P. Poodt,* Eindhoven University of Technology, Netherlands*; J. Hilfiker,* J.A. Woollam Co., Inc.*; E. Kessels, B. Macco,* Eindhoven University of Technology, Netherlands

Atmospheric-pressure *spatial* ALD (S-ALD) is a variant of conventional ALD which can achieve remarkably high deposition rates by moving the substrate at high speeds through different precursor zones that are spatially separated by an inert gas flow. The high through-put of S-ALD offers a great potential for scaling up the ALD processes, in particular, for green technologies such as photovoltaics, batteries and water electrolyzers. More than a decade of research on spatial ALD has led to successful application of S-ALD processes in industry. However to further commercialize S-ALD more material characterizations and process optimizations are needed to extend the material library of this method and introduce it to more applications.

In this work, we showcase the use of ultrafast *in-situ* spectroscopic ellipsometry (iSE) during S-ALD as a valuable tool for characterization and process development. *In-situ* metrology in general has been indispensable in conventional ALD for studying important aspects such as nucleation behavior and reaction mechanisms. Yet, for S-ALD such *in-situ* metrology is much less common, with a few reports on *in-situ* reflectometry, resistance measurements and exhaust gas analysis. This likely relates to the challenges associated with moving substrate, short timescales of cycles, and complicated geometry of the S-ALD reactor. However, *in-situ* metrology for S-ALD could help elucidate potential differences between conventional and spatial ALD due to e.g. widely different time- and pressure scales, and also help investigate unique aspects of S-ALD, such as co-injection of precursors for growth of compound materials. Additionally, using *In-situ* SE enables fast determination of saturations curves which significantly accelerates the process development.

Here we demonstrate that we can effectively perform iSE even for acquisition time of one second on our S-ALD tool using an ultrafast J.A. Woollam ellipsometer mounted adjacent to the deposition head. In terms of process development, we highlight that full saturation curves can be obtained in a single deposition run on a time scale of only a few minutes. Moreover, nucleation curve can be easily determined. This was done for common ALD processes for Al₂O₃, ZnO and SnO₂. Having this iSE method for S-ALD of conventional binary oxides established, current work focuses also on studying and comparing for example the deposition of ternary oxides using either supercycles or co-injection of precursors.

Area Selective ALD
Room Hall 3E - Session AS-TuM

Selective ALD

Moderators: Han-Bo-Ram Lee, Incheon National University, **Angel Yanguas-Gil**, Argonne National Lab

10:45am AS-TuM-12 A Novel SMI for AS-ALD, *Molly Alderman, A. Upadhyay,* Carleton University, Canada*; M. Griffiths, K. Blakeney, D. Agnew, P. Lemaire, J. Smith, D. Hausmann,* LAM Research*; S. Barry,* Carleton University, Canada*; D. Mandia,* LAM Research

Area selective atomic layer deposition (AS-ALD) presents a means to achieve the ever-increasing architectural density and decrementing feature sizes demanded by Moore's law beyond what is possible when patterning by photolithography alone. With inherently selective ALD processes being rare, the use of surfactants to promote or inhibit growth of films has gained traction.[1] In particular, small molecule inhibitors (SMIs) are preferable to self-assembled monolayers (SAMs) for modification of growth behaviour owing to their smaller size, improved thermal characteristics, vapour phase adsorption, and (when compared to the most common SAMs) lack of heavy heteroatoms, in particular sulfur, preventing film contamination.[2]

We have synthesized a family of novel polyfluorinated isonitriles with different chain lengths for use as a SMI in AS-ALD. As an example, Long Chain Inhibitor is readily synthesized in two steps from the amine and is volatile, with a 1 Torr vapour pressure at 33 °C. This compund shows promising selectivity for adsorption to metals over oxides as measured via quartz crystal microbalance (QCM), saturating gold with a surface density of 62 ng/cm² (0.81 molecules/nm²) with concurrently negligible adsorption on alumina (Figure 1). The synthesis and thermal characterization of several fluorinated isonitriles will be discussed. Their selectivity for metal surfaces

by QCM, as well as ToF-SIMS mapping on metal/SiO₂ patterned substrates will be shown to demonstrate selectivity, with excellent resolution provided by the high fluorine content of the molecule. Selective inhibition of zinc oxide ALD will also be discussed and selectivity values will be reported.

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11:00am AS-TuM-13 Atomic Layer Plasma Treatment for Area-Selective Atomic Layer Deposition of High-Quality SiO₂ Thin Film, *Sanghun Lee, S. Seo, T. Kim, H. Yoon, S. Park, S. Na, J. Seo,* Yonsei University, Republic of Korea*; W. Noh,* Air Liquide, Republic of Korea*; S. Chung, H. Kim,* Yonsei University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) has been intensively studied due to its demonstrated versatility in recent nanotechnology applications. The priority focus in AS-ALD is achieving the desired selectivity; thus, most studies to date have concentrated on the reaction mechanism of ALD on the growth/non-growth substrate or sought novel methodologies to resolve challenges in its implementation in high-volume manufacturing. On the other hand, the qualities of film deposited by AS-ALD were usually not highlighted. In this work, we studied the AS-ALD approaches that could enhance the selectivity and film quality simultaneously. We developed AS-ALD SiO₂ on SiO₂ whereas SiO₂ was not grown on SiNₓ. NH₃ plasma pre-treatment was employed to functionalize SiNₓ surface with more –NH species which are known for their lower reactivity toward Si precursors. The results show that NH₃ plasma pre-treatment is effective in increasing selectivity, but the plasma condition needs to be controlled to avoid inducing damage to the SiNₓ surface, which could offer reactive sites for precursor adsorption. We carried out ALD supercycle of NH₃ plasma pre-treatment and ALD SiO₂ to achieve higher selectivity. When the number of NH₃ pre-plasma treatment cycles was increased, the growth of SiO₂ on SiNₓ was further delayed. Furthermore, layer-by-layer NH₃ plasma pre-treatment densified the SiO₂ film owing to ion bombardment, as revealed in etching characteristics and x-ray reflection spectra. Moreover, NH₃ plasma pre-treatment did not result in incorporation of nitrogen into growing SiO₂ film as analyzed by x-ray photoelectron spectroscopy. Consequently, atomic layer NH₃ plasma pre-treatment enabled a higher selectivity and improved SiO₂ film quality, as evaluated by the electrical property measurement of metal-oxide-semiconductor capacitor.

11:15am AS-TuM-14 Enhancing Selectivity for AS-ALD of MoO₂ through Hydrogen Treatment: Strategy of Surface Cleaning and Expanding Deactivated Areas, *Hae Lin Yang, J. Kwon, C. Park,* Hanyang University, Korea*; S. Lee, B. Kim, C. Jung, H. Lim,* Samsung Electronics Co., Inc., Republic of Korea*; J. Park,* Hanyang University, Korea

Recently, in the field of DRAM capacitors, the demands for precisely depositing MoO₂ thin films for resolving the high leakage issue between high-k dielectric and TiN electrodes, onto TiN without additional patterning[1]. To meet these demands, Area selective atomic layer deposition (AS-ALD), which allows selective deposition on certain areas without undesired deposition on adjacent areas, is essential. Also accomplish the high selectivity of high-resolution films with high spatial resolution, the introduction of inhibitors is needed especially small molecular inhibitors (SMIs). SMIs consist of inert tail portions composed of single molecules, enabling them to have small sizes suitable for narrow lines at the nanometer scale. However, SMIs typically have short tail groups that cannot undergo van der Waals interactions, and they cannot densely cover the substrate surface due to steric hindrance from adjacent adsorbed SMIs during precursor adsorption[2]. Therefore, considerations regarding the treatment of unadsorbed areas and the removal of remaining reactive groups after SMI adsorption are necessary. To address this, we added a hydrogen treatment process during the AS-ALD process of MoO₂ using TCPS [C₆H₅SiCl₃] and DMA-TMS [(CH₃)₃SiN(CH₃)₂] as SMIs and analyzed the effects of hydrogen treatment on surface properties and selectivity using XPS, WCA, and AES mapping. Additionally, we calculated reaction energies for each adsorption step and final forms for each SMI-adhered surface using DFT and RSA simulations. TCPS, owing to its aromatic phenyl ring, covers a wider range of SiO₂ surfaces than DMA-TMS. However, only two out of three Cl ligands react, leaving about 1.4% of the remaining Cl ligands after

TCPS adsorption, increasing the surface energy and acting as adsorption sites for Mo precursors. However, by adding a hydrogen treatment cycle during the process, all remaining Cl ligands were removed, resulting in a 13° increase in WCA and a dramatic increase in selectivity from 61% to 96%. Furthermore, hydrogen treatment not only removed residual impurities but also reduced exposed -OH groups on the surface by converting them to -H, as confirmed by the results of hydrogen treatment added during the DMA-TMS process. Despite the absence of impurities to be removed, the WCA increased by approximately 7° after hydrogen treatment, and the selectivity also increased from 84% to 94.5%. In this way, appropriate treatments during AS-ALD processes, though simple, can effectively increase selectivity, enabling precise selective deposition in desired areas even in complex structures.

11:30am **AS-TuM-15 Contra-Selective Deposition of SiO$_2$ on Metals**, *Chad Brick, T. Ogata,* Gelest, Inc

In recent years, an increasing number of area selective processes have been developed for the deposition of dielectric films on dielectric layers. However, reports of the selective deposition of dielectric films on metal regions of a substrate are comparatively rare, typically involving the deposition of high-k dielectric films with significantly different chemistry with respect to the target low-k non-growth areas such as SiO$_2$ or SiN. In this study, a series of heteroatom-containing silanes with inherent selectivity towards metals over SiO2 and SiN and their conversion to SiO2 via plasma-enhanced atomic layer deposition have been investigated. It will be shown that under appropriate conditions, indefinitely thick films of SiO2 can be selectively grown on metals such as copper and cobalt with pre-existing native or thermal silicon dioxide as the non-growth substrate. Mechanisms of this unusual "contra-selectivity", with a film growing not only on a material other than itself with its unblocked self as a non-growth surface, but also continuing to grow to arbitrary thickness despite the near-identical nature of the growth and non-growth surfaces after the first few deposition cycles, will be discussed.

11:45am **AS-TuM-16 Photoluminescent Graphene-Lanthanide Heterostructures via Direct Laser Writing and Area-Selective Atomic-Molecular Layer Deposition**, *Aleksei Emelianov, K. Mentel,* University of Jyväskylä, Finland*; A. Ghazy,* Aalto University, Finland*; A. Johansson,* University of Jyväskylä, Finland*; M. Karppinen,* Aalto University, Finland*; M. Pettersson,* University of Jyväskylä, Finland

Area-selective atomic-molecular layer deposition (AS-ALD/MLD) is a promising "bottom-up" alternative to the current nanopatterning techniques [1,2]. It has been used on a variety of materials, including the growth of two-dimensional materials (2DM). While there are examples of AS-ALD being used on 2DM, the approach of combining it with AS-MLD is still mostly unexplored. Due to the inherent 2D nature, the surface of 2DM does not provide sufficient reactive sites for the chemisorption of ALD/MLD precursors compared with traditional microelectronics. Functionalization of certain surface areas is required to provide the selective growth of materials. Recently, we have overcome the chemical inertness of graphene to ALD precursors by local activation using direct femtosecond laser two-photon oxidation (TPO) [3] for selective ZnO deposition [4].

In this study, we guided the growth of Eu-organic thin films on top of single-layer graphene via TPO. We achieved high homogeneity and more than 90% selectivity in locally activated predefined regions for Eu films up to 15 nm. The polymer used for graphene transfer significantly affects the selectivity of the ALD/MLD process, as it might leave residues and promote unnecessary deposition in pristine graphene areas. The fabricated graphene/Eu-organic thin films exhibited high photoluminescence at 615 nm even when excited with a 532 nm laser. The films are suitable for various applications in optoelectronics, sensors, and LEDs.

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ALD Applications
Room Hall 3D - Session AA1-TuA

Energy: Solar Energy Materials II

Moderators: Arrelaine Dameron, Forge Nano, **Neil Dasgupta**, University of Michigan

1:30pm AA1-TuA-1 Toward All-ALD Halide Perovskite Solar Cells, *G. Popov, A. Weiss, M. Ritala, M. Leskelä, **Marianna Kemell**,* University of Helsinki, Finland **INVITED**

Halide perovskite solar cells show solar conversion efficiencies > 26 %, making them the most promising emerging photovoltaics technology. Halide perovskites have the general formula ABX_3 where most often A = $CH_3NH_3^+$, $CH(NH_2)_2^+$ or Cs^+, B = Pb^{2+} or Sn^{2+} and X = I^-, Br^- or Cl^-. Methylammonium lead iodide $CH_3NH_3PbI_3$ is a well-known example.

Commercialization of the halide perovskite solar cells is still impeded by challenges in upscaling. High quality perovskite layers can be made on small areas but the currently used methods are not suitable for large production volumes.

We have addressed the scalability issue by developing atomic layer deposition (ALD) processes for halide perovskites and other materials in perovskite solar cells. Our approach is based on ALD of binary halides, followed by their chemical conversion to the desired perovskites. As the first step, we developed ALD processes for the binary metal halides PbI_2 [1], CsI [2], SnI_2 [3], $PbCl_2$ [4] and $PbBr_2$ [4]. Prior to our work there were no ALD processes for iodides, bromides or chlorides. Using the binary halides as the starting points, we can deposit the halide perovskites $CH_3NH_3PbI_3$ [1], $CsPbI_3$ [2] and $CsSnI_3$ [3]. ALD-PbI_2 film is converted to $CH_3NH_3PbI_3$ by exposing it to CH_3NH_3I vapor, whereas ALD-CsI film can be converted into $CsPbI_3$ by exposing it to the ALD process of PbI_2, and to $CsSnI_3$ by exposing it to the ALD process of SnI_2. Combining these with the ALD processes of $PbCl_2$ and $PbBr_2$ enables compositional engineering as a route to fine-tuned properties.

In a halide perovskite solar cell, the perovskite layer is sandwiched between n- and p-type semiconductor films. ALD processes for various n-type materials are readily available, whereas p-type materials are more challenging. We have developed low-temperature ALD processes that enable deposition of p-type PbS [5] on $CH_3NH_3PbI_3$ at temperatures below 100 °C, without damaging it. Furthermore, the PbS film also protects the $CH_3NH_3PbI_3$ film from degradation under ambient conditions, acting thus in a dual role as a functional layer and as an encapsulant. We have also developed a two-step process for p-type CuI [6] that is compatible with $CsPbI_3$. Our processes form the first steps towards making complete halide perovskite solar cells by ALD-based methods.

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2:00pm AA1-TuA-3 Plasma-enhanced Atomic Layer Deposition of Tunable Cobalt Nitride Thin Films Enabled by Sequential N_2 Plasma Exposure, ***Matthias Kuhl**,* Technical University Munich, Germany*; L. Kohlmaier,* Technical University Munich, Austria*; I. Sharp,* Technical University Munich*; J. Eichhorn,* Technical University Munich, Germany

Transition metal nitrides form an interesting class of materials due to their mechanical hardness, tunable electronic and magnetic properties, and catalytic activity. In this context, cobalt nitride is a promising material both in the semiconductor industry and for electrochemical (EC) energy conversion. Despite these potential applications, there are limited reports on depositing cobalt nitride via atomic layer deposition (ALD), especially at lower temperatures (<200 °C). Such low temperature processes would provide enhanced processing compatibility, including for photolithography, and aid in preserving high quality light absorber/catalyst interfaces for photoelectrochemical (PEC) energy conversion applications.

Here, we report on the low-temperature (100 - 200 °C) plasma-enhanced (PE) ALD of cobalt nitride using cobaltocene $CoCp_2$ as precursor and either NH_3 plasma or H_2/N_2 plasma as co-reactant. The deposition at low temperatures is enabled by introducing a subsequent N_2 plasma pulse at the end of each PE-ALD cycle to regenerate surface sites for the subsequent precursor adsorption. We analyze the film growth characteristics and material properties by in-situ spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Varying deposition temperature and plasma gas composition can be leveraged to tune the Co/N ratio and thus the material properties from semiconducting to metallic. Lastly, we applied the thin films as heterogeneous catalysts for the EC oxygen evolution reaction. Overall, this work highlights the use of PE-ALD as a promising approach for depositing metal nitrides with tunable film properties at low temperatures.

2:15pm AA1-TuA-4 Hybrid Solar Cells Comprising Inorganic and Organic Materials Through Vapor Phase Infiltration, *K. Ashurbekova,* 1. CIC nanoGUNE, Spain*; **Mato Knez**,* CIC nanoGUNE, Spain

Inorganic, organic and perovskite solar cells (SCs) have witnessed unprecedented progress in the past decade. Perovskite SCs, while highly efficient, encounter stability and toxicity concerns. Inorganic SCs excel in efficiency and durability but lack flexibility, prompting exploration of alternative technologies. In contrast, organic SCs offer flexibility, facing lower efficiency challenges. Despite the inherent limitations of each SC type, they have their own merits, promising a grand step forward if synergy is achieved. Combining the adaptability of organic SCs with the efficiency of inorganic ones may yield a hybrid versatile alternative. We are introducing new hybrid solar cell materials by applying vapor phase infiltration (VPI) to polymers.

We present a new hybrid materials set obtained after growing Sb_2S_3 and Sb_2Se_3 by VPI inside the bulk and atop of diverse polymers including poly(triaryl amine) (PTAA), Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD), Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and Poly(3-hexylthiophene-2,5-diyl) (P3HT). PTAA, PolyTPD and PEDOT:PSS are excellent hole-transporting semiconducting materials, while P3HT is an efficient light absorber in the visible range. Metal chalcogenide light absorbent materials, such as Sb_2S_3 and Sb_2Se_3, have huge potential in photovoltaics owing to the suitable bandgap of 1.7 and 1.3 eV, and high light absorption coefficient above 10^4 and 10^5 cm^{-1}, respectively. For the VPI growth of Sb_2S_3 and Sb_2Se_3, $SbCl_3/H_2S$ and $SbCl_3/(Me_3Si)_2Se$ precursors were used, respectively. The hybridization process was monitored *in-situ* with a Quartz Crystal Microbalance (QCM). The monitoring allowed studying the saturation behavior of the VPI process and quantitatively controlling the loading of the inorganic precursors into the polymer. Scanning electron microscopy (SEM) showed infiltration in form of Sb_2S_3 and Sb_2Se_3 crystal growth throughout the whole polymer depth. TEM was used to examine the structure of the crystalline phase of the Sb_2S_3 and Sb_2Se_3 grown in the bulk and on top of the polymer. A complete photovoltaic characterization of a new set of hybrid materials, including thecurrent density–voltage (J–V) characteristic of SCs under illumination, power conversion efficiencies (PCEs) and the external quantum efficiency (EQE) of a device, was performed in 16 ITO pins SCs. Planar p-i-n SCs devices of the following structures were fabricated: ITO glass/polymer-Sb_2S_3//Sb_2Se_3 /ETL/Ag and ITO glass/polymer-Sb_2S_3//Sb_2Se_3/perovskite/ETL/Ag. C60/BCP was used as an electron transport layer (ETL). The results offer new solutions for sustainable solar energy.

2:30pm AA1-TuA-5 Mitigating the Cross-Ion Migration Towards Perovskite Using a Conformal Layer of Alumina via Atomic Layer Deposition, *Mayank Kedia, C. Das, M. Saliba,* Forschungszentrum Jülich GmbH, Germany

Atomic layer deposition (ALD) of aluminum oxide (Al_2O_3) layers is an established technique for encapsulation and stabilization of active materials against environmental stressors. This is particularly important for sensitive perovskite materials, that react with moisture, light, O_2, etc. during the device operation conditions. [1] At the same time, the role of the ALD-Al_2O_3 barrier layer between the perovskite and charge transport material still requires further analysis.

In this study, we demonstrate the surface coverage uniformity of a <1nm ALD-Al_2O_3 layer on bare perovskite at room temperature. [2] Such a sub-nanometer ALD-Al_2O_3 coverage on the different perovskite facets reduces surface defects enhancing the device performance from 19.2% to 20.1%. This ultra-thin layer of ALD-Al_2O_3 acts as a barrier layer for the diffusion of degraded byproducts of the aged spiro-OMeTAD preventing perovskite's transition to amorphous phases. Consequently, the ALD-Al_2O_3-based device retains 75% of its initial power conversion efficiency as compared to 10% for pristine devices after 180 days of shelf-aging, followed by 1000 min of maximum power point tracking under ambient conditions. Finally, this study deepens the mechanistic understanding of the ALD-Al_2O_3 as an impermeable layer, highlighting the multifaceted role of buffer layers in interface engineering.

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2:45pm AA1-TuA-6 Thermoelectric Properties of Sb_2Te_3-based Ferecrystals based on Atomic Layer Deposition, *J. Yang, D. Shin, S. Lehmann, A. Bahrami, Korneli Nielsch,* Leibniz Inst. of Solid State and Materials Research / IFW-Dresden, Germany

Atomic layer deposition is a very versatile technology for the deposition of thin films with precise thickness control on large areas, non-planar surfaces and 3D objects. The chemical reaction is surface limited, well defined and works in most cases at low temperatures (RT to 250 °C). For a number of classical van der Waals 2D materials, there have been reports on ALD of transition metal dichalcogenide (TMDC) of MoS_2, SnS_2, WS_2 and WSe_2, which also included the electronic characterization as a field effect transistor (FET).

In this work, we have fabricated by atomic layer deposition (ALD) multilayers of layered materials based on topological insulators and van der Waals materials, called *ferecrystals*. These ferecrystals can be tailored to exhibit unusual properties such as high electrical conductivity or low thermal conductivity or magnetic properties. A detailed ferecrystal study was performed on ferecrytals of Sb_2Te_3 and SbO_x, which has been grown at the same temperature as single layers of Sb_2Te_3. Without post-annealing, the electrical and thermoelectric characterisation of the highly ordered samples have been performed with the ZT-chip setup. In general, the carrier mobility is very high >150 Vs^2/cm^2 and is even improved when the thickness of the Sb_2Te_3 layers is reduced and the number of SbO_x layers (typically 2 nm thickness) is increased. Detailed XRD investigations have been performed and an enhanced crystalline order is observed in the ferecrystal system compared to individual layers of Sb_2Te_3. We have grown ferecrystals based on Sb_2Te_3 and Sb_2Se_3 with tetrahedral and orthorhombic crystal structure, respectively. The p-type hole carrier concentration of Sb_2Te_3 films can be enhanced through the sublayer doping of Sb_2Se_3. The highest carrier concentration achieved was 2.5×10^{19} cm^{-2} when the thickness ratio of Sb_2Te_3 to Sb_2Se_3 was (4 nm/2 nm). Further reduction of the Sb_2Te_3 thickness resulted in a high Seebeck coefficient of 172 µV/K at room temperature.h

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3:00pm AA1-TuA-7 Atomic Layer Deposition for Photoelectrochemical Solar Fuel Production, *Lionel Santinacci,* CNRS/Aix-Marseille Univ., France
INVITED

Since H_2 is now considered as a key energy vector, its production through water electrolysis coupled to a renewable power supply is envisioned as a large-scale production scheme. In parallel to the various electrolysis approaches, H_2 and O_2 production from H_2O photoelectrolysis appears to be a more straightforward process. It has opened an attractive, though challenging, field of investigations that ultimately tackles direct water dissociation using an unbiased photoelectrochemical cell (PEC) under sunlight: solar fuel production. The recent remarkable conversion yield of 19%,[1] reported on unbiased PEC built with expensive and unstable III-V semiconductors (SCs) associated to platinoid catalysts, is very promising but the H_2 production remains more expensive than from fossil sources . The field needs therefore to significantly improve yield, stability and cost.

In the recent years, it has been shown that ALD can play a valuable role to address such challenges. Photoelectrodes can be significantly improved by (i) surface structuring inducing a better light harvesting and a higher active surface area, (ii) by co-catalysts improving the reaction kinetics and enhancing the photocurrent and (iii) by protective films extending the electrode lifetime. ALD exhibits key advantages to achieve such improvements and recent literature has shown numerous successful examples of photoelectrode modifications. ALD is, indeed, known to be well-suited to conformally coat nanostructured surfaces with either continuous pinhole-free layers or uniform particle collections. After a short reminder on the basics of water photosplitting (principle, materials of interest and current challenges), this review will therefore show how ALD can be implemented in the field. Although it is a minor application, specific materials can be synthesized by ALD but the mains uses of this technique consist of fabricating nanostructured electrodes, deposit co-catalysts, passivate or modify the semiconductor/electrolyte junctions and prevent corrosion. In most cases, materials combination is the appropriate way to reach better performance and durability and ALD is, of course, a good tool for such approach.

[1] W.-H. Cheng et al, ACS Energy Lett. (2018) 3, 1795

ALD Applications
Room Hall 3D - Session AA2-TuA

Energy: Catalysis and Fuel Cells
Moderators: Riikka Puurunen, Aalto University, Finland, **Ruud van Ommen**, Delft University of Technology

4:00pm AA2-TuA-11 ALD Young Investigator Award Finalist Talk: How Instability Can Be Beneficial for Electrocatalysis: The Case of Nickel Sulfide Oxygen Evolution Reaction Precatalyst, *Miika Mattinen,* University of Helsinki, Finland*; J. Schröder, G. D'Acunto, T. Jaramillo,* Stanford University*; M. Burke Stevens,* SLAC National Accelerator Laboratory*; M. Ritala,* University of Helsinki, Finland*; S. Bent,* Stanford University

Water electrolysis is a key technology in building a sustainable world based on renewable energy. Hydrogen gas (H_2) produced by water electrolysis can be used, for example, as a fuel and reactant in diverse industries including chemical and steel manufacturing. Of the two half-reactions occurring inside water electrolyzers, the oxygen evolution reaction (OER) limits the efficiency. Thus, development of highly active, stable, and affordable OER catalysts is critical. Nickel-iron metal alloys, oxides, and hydroxides are among the most active OER catalysts in alkaline electrolytes. Their activity is attributed to oxyhydroxide species formed under OER conditions.[1] Recent studies looking at other promising Ni compounds such as NiS_x have found them, too, to transform to oxyhydroxides. Thus, all the Ni(Fe)-based catalysts listed above may be described as precatalysts to the active oxyhydroxide.[2] However, the effect of the precatalyst material on the activity and structure of the active catalyst as well as the role of electrolyte impurities (e.g. Fe) remain poorly understood.

To answer these questions, we deposited crystalline NiS_x (β-NiS with traces of Ni_9S_8) thin films by ALD using $NiCl_2(TMPDA)$ (TMPDA = *N,N,N',N'*-tetramethyl-1,3-propanediamine) and H_2S at 165 °C. The ALD NiS_x films were compared to NiO, $Ni(OH)_2$, and Ni precatalysts deposited on SnO_2:F electrodes by ALD and other methods. Electrochemical measurements in 0.1 M KOH (purified from iron) and X-ray photoelectron spectroscopy revealed that all the precatalysts convert to an oxidized phase ("NiOOH") under OER conditions, yet at substantially different rates ($NiS_x ≈ Ni(OH)_2$ >> Ni > NiO). Fast conversion is beneficial for achieving high current densities. We are investigating the structure of the formed oxidized phase using *operando* X-ray absorption spectroscopy.

Iron impurities in the KOH electrolyte incorporate into the (pre)catalysts reaching up to 30 metal-%. This added iron greatly increases the OER activity and stability of the catalysts. Compared to synthesis of multimetal catalysts, incorporating iron from the electrolyte simplifies synthesis and can accelerate the conversion to the active catalyst. The highest iron concentration and best OER performance is found for the fastest converting precatalysts, i.e. NiS_x and $Ni(OH)_2$. Understanding of the structural evolution of OER precatalysts together with the conformality of ALD enables engineering of high-performance electrodes for alkaline electrolyzers.

1 Burke et al., *Chem. Mater.,* 2015, **27**, 7549

2 Kawashima et al., *Chem. Rev.*, 2023, **123**, 12795

4:15pm AA2-TuA-12 Diffusion–Reaction Modeling for Atomic Layer Deposition on Spheres: Comparison with Experimental Data, *Niko Heikkinen,* VTT Technical Research Centre of Finland*; J. Yim, J. Järvilehto,* Aalto University, Finland*; S. Saedy,* Delft University of Technology, Netherlands*; P. Brüner, T. Grehl,* IONTOF GmbH, Netherlands*; E. Haimi, J. Velasco, C. Gonsalves,* Aalto University, Finland*; R. van Ommen,* Delft University of Technology, Netherlands*; J. Lehtonen,* VTT Technical Research Centre of Finland*; R. Puurunen,* Aalto University, Finland

Diffusion–reaction (DR) modeling is a powerful tool to estimate reactant travel and film formation in atomic layer deposition (ALD) in high-aspect-ratio (HAR) features [1]. The modeling work of conformality evolution on (modelling-wise) one-dimensional features (circular pores and channels) has been extended to porous materials described by an average pore size, tortuosity and porosity, still keeping the geometry one-dimensional through considering the slab geometry [2]. While a slab can describe well the case of planar surfaces (e.g. membranes), typically particles used as catalyst supports resemble more spheres or cylinders.

We have recently extended ALD diffusion–reaction modeling to describe spheres and cylinders in addition to slabs [3]. Our study showed for example that the reactant exposure requirement for full saturation increases in the order spheres < cylinders < slabs.

Here, we extend the earlier theoretical work [3] and compare modeling to experimental studies on high-surface-area alumina spheres. Two case examples are presented: zinc on alumina using the recently reported $Zn(acac)_2$ reactant [4] (one reaction step in a fixed-bed reactor, with $Zn(acac)_2$ dose varied), and platinum on alumina using the well-known $MeCpPtMe_3$ reactant (5 cycles with oxygen as counter-reactant, in a fluidized bed reactor, with exposure time varied). Alumina spheres with diameters of 1, 1.8 and 2.5 mm were employed, with a specific surface area on the order of 200 m^2/g. Modelling results are found to agree reasonably well with the experimental data.

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[3] N. Heikkinen, J. Lehtonen, R. L. Puurunen, Physical Chemistry Chemical Physics, accepted (2024).

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4:30pm AA2-TuA-13 Highly Durable Pt Based Fuel Cell Catalysts via Atomic Layer Deposition, *Xiao Liu, H. Liu, Y. Gao,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; B. Shan,* State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

The activity and durability of carbon supported Pt based electrocatalysts (Pt/C) are unchanging goals for the widespread application of hydrogen fuel cells. Under the harsh operation conditions of fuel cell, pure Pt nanoparticles (NPs) suffer from great electrochemical dissolution, leading to serious stability decay. To address this challenge, overcoating Pt NPs with organic capping agent, polymer layers, inorganic carbon-based nanoshell or metal oxide (MO_x), nitride has been recognized as a prospective strategy to prevent the direct exposure of Pt surface. Atomic layer deposition (ALD) is known for its atom-level control accuracy over the film growth on substrates or NPs based on self-limiting chemical half-reactions. Herein, an effective strategy is developed to improve the activity and durability of Pt catalyst for hydrogen fuel cell based on atomically surface and interface modification on Pt nanoparticle, which is a promising scale-up approach via selective atomic layer deposition. Selective ALD of metal oxides such as TiO_2, ZnO, SnO_2 have been performed on Pt/C electrocatalysts by a custom-made fluidized-bed reactor. The behavior of selective deposition is controlled by the reactor temperature, oxygen source and number of ALD cycle. Following post treatments such as nitriding and high temperature reduction are performed to precisely control the surface structure of supported Pt nanoparticles. The activity and durability of Pt based electrocatalysts have been enhanced via selective ALD and following post treatment. N doped TiO_2 (N-TiO_2) is demonstrated to selectively deposit on the low coordination sites of Pt NPs and expose (111) facet without changing their size distribution and wasting the electrochemical active surface area. The selective decoration of N-TiO_2 could effectively inhibit the intrinsic degradation of Pt NPs and prevent the electrochemical sintering during accelerated durability tests. Besides, the intrinsic activity of Pt NPs is also enhanced based on ultra-thin ZnO coating. The prepared uniform PtZn intermetallic nanocrystals with the size of 2.50 ± 0.65 nm achieve outstanding single-cell performance with the mass activity of 0.48 A $mgPt^{-1}$ at 0.9 V and 10.42% loss of mass activity after 30000 voltage cycles, which is superior to commercial Pt/C. The enhanced activity and durability is attributed to the decreased binding energy of Pt-oxygen intermediates for weakly polarized surface Pt atoms and suppressed electrochemical Ostwald ripening.

4:45pm AA2-TuA-14 Catalyst on Top? Importance of the Final Layer of an ALD Deposited Catalyst. Ni-Fe Catalysts Deposited by ALD, *Ruben Blomme,* Ghent University, Belgium*; R. Ramesh,* Ghent University, Belgium, India*; L. Henderick, M. Minjauw, P. Vereecke, M. Adriaens, C. Detavernier, J. Dendoven,* Ghent University, Belgium

H2 is considered a crucial energy carrier in the transition to a more sustainable future. It serves as an essential feedstock for many industries and can also be used as an alternative, low-emission fuel for keyindustrial processes, such as steel production. However, the renewable method to produce H2, viawater electrolysis, is currently uncompetitive compared to the fossil fuel-based alternative.

One aspect in which the efficiency of water electrolysis can be improved is through the development of effective catalyst materials. Currently, noble metal-based catalysts are utilized for H2 production, but this approach is not sustainable in producing the required amount of H2 due to the high cost and scarcity of these metals.

To address this, alternative catalysts are under development, with some of the more promising materials being transition metal oxides and phosphates. The use of Atomic Layer Deposition (ALD) allows for the precise control during the catalyst production process, including conformal layer-by-layer control and compositional tailoring. Previous works on ALD development of metal phosphate materials, such as iron[1], nickel[2], and cobalt[1,3], have demonstrated their viability and effectiveness as Oxygen Evolution Reaction (OER) catalysts.

In this study, a series of Ni-Fe mixed phosphate materials were deposited via a supercycle approach and quantified for their electrochemical performance. Notably, during the deposition process, there was a preferential incorporation of Ni over Fe across all measured samples (Fig. 1). According to X-ray fluorescence (XRF) measurements, the effectiveness of one NiPO ALD cycle in a NiPO – 4 FePO process is twice that of the same ALDcycle in a pure NiPO deposition.

The order of the ALD processes in the supercycle recipe and the overall film thickness had significant impact on the performance as a catalyst material. The most noteworthy effect of customizing the ALD sequence was observed when the cycle sequence in the supercycle was reversed to ensure FePO was deposited as the final layer (Fig. 2). This resulted in an overall potential gain of 20 mV (at 10 mA/cm^2) for materials with identical composition.

By increasing the thickness of the deposited layer, additional gains could be achieved. These findings align with previous reportsthat observed the restructuring of cobalt phosphate materials to oxides/hydroxides with a significantly increased electrochemical active surface area[4].

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**5:00pm AA2-TuA-15 Enhanced Oxygen Evolution Reaction Catalysts by PE-ALD: Atomically Dispersed Co_1 and Fe_1 Supported on Ultra-thin Films of Doped NiO_x, *Ina Oestroem,* University of New South Wales, Australia*; M. Favaro,* Helmholtz Zentrum Berlin, Germany*; P. Burr, B. Hoex,* University of New South Wales, Australia

Hydrogen production through water splitting is hindered by the anodic oxygen evolution reaction (OER), which has a complex, sluggish mechanism leading to a high overpotential.Nickel oxide-based catalysts (NiO_x) are a

highly active, cheaper alternative to the precious metal catalysts of IrO_2 and RuO_2. Plasma-enhanced atomic layer deposition (PE-ALD) is a powerful tool for optimising thin films to increase OER activity. This work employs PE-ALD, using O_2 and H_2 plasma, to atomically disperse Co_1, Fe_1, and Fe_1Co_1 at the surface of thin films of $SnNiO_x$. The films were conditioned by 600 cycles of cyclic voltammetry (CV) at 20 mV/s, testing their stability and formation of the catalyst OER-active structure. Electrochemical Impedance Spectroscopy (EIS) was employed (0.1 – 10^4 Hz and 1.5 – 1.7 vs RHE), after 20 cycles, and at the end of the 600 cycles, to investigate the changes in double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}). The apparent activity was studied with linear sweep voltammetry (LSV) at 1 mV/s, and the durability by chronopotentiometry (CP) at 10 mA/cm^2 for 12 hrs. The 12 hr CP tests were followed by rest and another CP for 1 hr, showing further improvements in activity after a recovery period. The turn-over frequency (TOF) at different potentials was obtained through redox peak integration and C_{dl}. Our results show that atomically dispersed Co_1 and Fe_1 produced via H_2 plasma, in contrast to an O_2 plasma, further improved the OER activity of thin films of $SnNiO_x$. The best OER catalyst is $Fe_1Co_1/SnNiO_x$ with 284 mV of overpotential at 10 mA/cm^2 on FTO, compared to 320 mV for Ru on glassy carbon (GC) in 1M NaOH, with remarkable stability and durability after prolonged CP test. Tafel analysis and EIS suggest the improved performance is due to a lower R_{ct}. All-electron hybrid Density functional theory (PEB0/pob-TZVP) provided insights into the thermodynamics of the OER mechanism and electronic properties of the catalysts. X-ray diffraction, X-ray photoelectron spectroscopy, and soft X-ray absorption characterised the atomic structure, active sites oxidation state and coordination environment. The morphology and conformality were analysed with atomic force microscopy (AFM), scanning tunnelling electron microscopy (STEM), and spectroscopic ellipsometry (SE). This work shows that the OER activity of $SnNiO_x$ can be improved by atomically dispersed Fe_1Co_1 by PE-ALD and that the catalysts are stable after prolonged CP tests. Our study highlights PE-ALD as a promising technology for optimising low-cost catalysts with high atom economy and atomic-level precision.

5:15pm AA2-TuA-16 Optimization of Photocurrent Response of Atomic Layer Deposited $Ti_xFe_{2-x}O_3$ Photoanodes, *Anjan Deb*, A. Vihervaara, G. Popov, M. Chundak, M. Heikkilä, M. Kemell, M. Ritala, M. Putkonen, University of Helsinki, Finland

Hematite (α-Fe_2O_3) has attractive properties, such as a low band gap energy (1.9-2.2 eV), abundant availability and high chemical stability, for photoelectrocatalytic applications such as water splitting and organic micropollutant decomposition (Liu, et al., 2023). However, it has also several limitations, including low optical absorption coefficient and a short minority carrier diffusion length ranging from 2-4 nm. To address this intrinsic problem of hematite, researchers are exploring the use of nanoscale fabrication techniques and doping with aliovalent cations, such as Ti^{4+}, as a potential solution. Atomic layer deposition (ALD) is a promising technique that enables the deposition of pinhole free thin films with precise atomic-level composition and thickness control over an extensive surface area and high aspect ratio surfaces (Leskelä & Ritala, 2002).

In this study, we employed response surface methodology (RSM) based face-centred central composite design (FC-CCD) for modelling and optimization of photocurrent response of $Ti_xFe_{2-x}O_3$ thin film photoanodes grown by ALD. Two ALD process, $FeCp_2$ + O_3 and $Ti(OMe)_4$+H_2O, were combined to grow the $Ti_xFe_{2-x}O_3$ thin film photoanodes. Deposition parameters such as total number of ALD cycles (film thickness), cycle ratio of TiO_x to FeO_x (the dopant concentration) and deposition temperature were chosen as the independent factors while the photocurrent densities (PCD) at 1.23V and 1.70V vs RHE were considered as response. Thin film depositions were carried out according to the FC-CCD design matrix (Figure 1-a) based on the level of experimental factors presented in Table 1. After deposition, all the films were subjected to annealing at 500°C for 1 hour in air and evaluated for photocurrent response using a photoelectrochemical cell under standard illumination of AM 1.5G, 100 mW/cm^2. Linear sweep voltammetry (LSV) method was used to record the photocurrent responses at 1.23 and 1.70V vs RHE (Figure 1-b) at water oxidation conditions (pH ≈ 13.2).

After fitting the experimental data to the second-order polynomial equation, a mathematical model was developed that correlates the experimental variables with the response. The analysis of model parameters indicates that film thickness and dopant concentration are the most important elements that govern the PCD of $Ti_xFe_{2-x}O_3$ photoanode. The predicted PCD values using the model equations agreed well with the experimental data (R^2=0.95 for PCD@1.23V and R^2=0.98 for PCD@1.7V vs RHE) as shown in Figure 2. This study demonstrated the effectiveness of

RSM based modelling to predict the photocurrent response of photoelectrode materials.

ALD Fundamentals
Room Hall 3A - Session AF1-TuA

Precursors and Chemistry: Precursor Design, New Precursors, Process Development III

Moderators: Anjana Devi, Ruhr University Bochum, **Paul Williams**, Pegasus Chemicals

1:30pm AF1-TuA-1 New Class of Tin Precursors Targeting Low Temperature ALD Processing, *Jean-Pierre Glauber*, A. Devi, Ruhr University Bochum, Germany

Motivated by the ever-increasing interest for low temperature atomic layer deposition (ALD) processes of tin-based nanomaterials to implement them in flexible devices or sensitive material stacks, new precursors with prerequisites for ALD are of key interest. Although several tin precursors have been reported, low temperature processing require a distinct reactivity to ensure a clean ligand cleavage at the targeted moderate process conditions.[1-4]

All-nitrogen coordinated chelating ligands with several metals have garnered increasing scientific attention while they impart reactivity and suitable thermal stability because of the chelating effect. Among them, amidinate based complexes such as tin(II)amidinates and tin(II)formamidinates have been in the focus, but their strong binding nature can lead to insufficient ligand cleavage leading to impurities in the thin films.[1-4] This can be attributed to their delocalized electron ligand-metal system that significantly increases their stability, but could make complete ligand cleavage difficult, especially when moderate process conditions are targeted.

To tackle this issue, alternative chelating ligand systems such as geminal diaminosilane (gDAS) are promising alternatives as demonstrated for several metals including Co, V, Ni and Mg.[1,5] In this study, a systematic variation of the gDAS ligand side chains resulted in tin compounds [Sn(tBu–gDAS)$_2$] (**1**) and [Sn(gDAS)$_2$] (**2**) which were characterized thoroughly by complementary analytical methods including NMR, FTIR, EA, SCXRD, EI-MS and LIFDI-MS. The monomeric nature of the complexes was confirmed by LIFDI-MS measurements and SCXRD. Thermal analysis and vapor pressure determination revealed favorable volatility. This study reveals, that the distinct changes in the ligand side chain can have significant influence on their respective thermal behavior. The encouraging thermal properties of the complexes makes them appealing for application in low temperature ALD processes of tin-based nanomaterials which is exemplified with ALD of SnO_x.

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1:45pm AF1-TuA-2 Novel Synthesis Route for Atomic Layer Epitaxy of $BaSnO_3$, *Andreas Alstad*, H. Sønsteby, University of Oslo, Norway

Since 1965 Moore's law has predicted the development of transistor density for decades, but silicon-based devices are reaching their physical limits. Even HfO_2, a high-κ dielectric which replaced the SiO_2 gate oxide in 2007, will soon meet the same fate. New materials are thus needed to further evolve electronic devices with regards to performance and industrial feasibility. An emerging class of materials that may bring about a new paradigm of device design are complex oxides. Their cations can easily be substituted via doping to alter and tune their electronic properties. The research on these materials in the context of microelectronics has barely scratched the surface, as there are numerous atomic configurations of ternary oxides yet to be explored. If one considers quaternary oxides and beyond, then the possibilities border on countless. Nanoscale electronic devices are extremely sensitive to impurities and defects, which is why atomic layer deposition (ALD) is increasingly being used in manufacturing to ensure uniformity and conformality. One promising candidate in this paradigm shift is the perovskite $BaSnO_3$ (BSO). BSO is a transparent wide-bandgap n-type semiconductor that has gotten attention for its excellent charge carrier mobility, especially when doped with lanthanum, making it a promising candidate for high-frequency electronics and other applications

where good charge carrier transport is important. It also shows excellent thermal stability.

Designing an ALD process for BSO and characterizing it is the topic of this work. The ALD processes for SnO_2 and BaO have been optimized separately both at a deposition temperature of 300 °C. X-ray fluorescence spectroscopy of our SnO_2 films using $Sn(IV)Cl_2(acac)_2$ found no chlorine impurities in the film. Additionally, we have demonstrated gas sensing capabilities of our SnO_2 thin films. The deposited barium films using $Ba(^iPr_3Cp)_2$ contain both $BaCO_3$ and BaO, confirmed by Fourier-transform IR spectroscopy. The next step is to tune the stoichiometry of the ternary ALD process. Combining these into BSO thin films likely requires post-deposition annealing to decompose and remove the carbonate. The last deposition will attempt epitaxial growth of BSO on a $SrTiO_3$ substrate. Finally, we will investigate the electronic properties of BSO as function of its thickness, such as charge carrier mobility.

$BaSnO_3$ sees potential uses in microelectronics as a transistor channel material for its mobility, but also in photovoltaics as an electron transport layer (ETL) to reduce the probability of electron-hole recombination, and as a transparent conducting oxide (TCO) for displays and touch screens.

2:00pm AF1-TuA-3 Microwave Enhanced ALD of Al_2O_3, B. Kupp, A. Schraner, John Conley, Oregon State University

While advantageous for many applications, the low deposition temperature characteristic of ALD can allow incorporation of -OH groups or residual impurities from unreacted ligands leading to non-ideal stoichiometry and sub-optimal physical, optical, and electrical properties. Although increasing deposition temperature and post deposition annealing can help drive off impurities, increase density, improve stoichiometry, adjust morphology, and improve properties of ALD films, these strategies can move a process out of the ALD regime or exceed the thermal budget of sensitive substrates or devices, respectively. To maintain the low thermal budget of ALD while maximizing film properties, annealing or adding energy *during* each (or every few) ALD cycle or supercycle can help drive/speed reactions and reduce impurity/ligand incorporation. Energy enhanced (EE)-ALD methods to date include in-situ rapid thermal (MTA, DADA, etc.) annealing, flash lamp, plasma exposure, and UV, and electric field [1-15].

Here, we introduce microwave enhanced (MWE) ALD using an MKS SG 1024 solid state microwave (MW) generator with a custom antenna integrated into a Picosun R200 PEALD. Al_2O_3 films were deposited at 300 °C using TMA and H_2O. Thickness was measured using a Film Sense FS-1 mapping ellipsometer. Adding a 30 s in-situ 400 W MW exposure (without plasma generation) during the TMA purge part of each ALD cycle reduced film thickness by ~2% across a 150 mm Si wafer (Fig. 1). Preliminary leakage measurements on MOS devices suggest an associated reduction in low field leakage (1 MV/cm) and decrease in the onset-voltage for Fowler-Nordheim conduction. Additional results to be presented include placement of MW exposure step within ALD cycle, temperature, electrical data, morphology, and other materials. MWE-ALD merits further investigation as an EE-ALD technique.

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2:15pm AF1-TuA-4 Atomic Layer Deposition of SnO Film Using Liquid $Sn(EtCp)_2$ Precursor and Combinations of H_2O and H_2 Plasma, Fumikazu Mizutani, N. Takahashi, Kojundo Chemical Laboratory Co., Ltd., Japan; T. Nabatame, National Institute for Materials Science, Japan

The SnO_2 (Sn^{4+}) and SnO (Sn^{2+}) films have been widely investigated as n-type and p-type oxide semiconductors, respectively, for oxide TFTs. We previously reported characteristics of SnO_2 films deposited by ALD using a new Sn precursor (bis(ethylcyclopentadienyl) tin; $Sn(EtCp)_2$) and O_2 plasma [1]. In this study we investigated SnO films formation by ALD with the same $Sn(EtCp)_2$ and combination of a weak oxidant H_2O and a strong reduction H_2 plasma gases.

At first, the usefulness of H_2O gas on formation of the SnO film during ALD with $Sn(EtCp)_2$ was studied. The growth temperature was 200 °C and ALD cycle was 100. Surprisingly, no growth of SnO film was observed because the thickness of the SnO film was less than 1 nm regardless of the number of ALD cycle. This was quite different results from our previous research of ALD of ZnO using a similar two-coordinated cyclopentadienyl complex and H_2O [2]. This was thought to be due to insufficient adsorption of $Sn(EtCp)_2$ on the SnO surface.

To solve this problem, we investigated ABC type ALD in which H_2 plasma treatment is applied to the SnO surface so that $Sn(EtCp)_2$ is well adsorbed. ALD process was conducted by using $Sn(EtCp)_2$ as a precursor and H_2O followed by H_2 plasma as co-reactants. SnO films were deposited on 150 mm Si wafers with native oxide films at a growth temperature of 200 °C. Saturation of reaction was confirmed when 0.2 s of $Sn(EtCp)_2$, 3 s of H_2O, and 5 s of H_2 plasma pulse times were applied. At this condition, linear growth of SnO film was observed, and the growth per cycle (GPC) was approximately 0.05 nm/cycle. This GPC is relatively high compared to the previously reported values for ALD of SnO [3]. Note that the high GPC shown in Ref. [3] is the value under low growth temperature conditions, and the GPC at a growth temperature of 200 °C is quite low at about 0.01 nm/cycle.

SnO thin films were deposited by ALD using a new cyclopentadienyl-based precursor and combinations of H_2O and H_2 plasma. Linear growth with high GPC of SnO thin film was confirmed.

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2:30pm AF1-TuA-5 A New Water Assisted ALD Process for Sc_2O_3 Using a Volatile Liquid Precursor, Martin Wilken, Ruhr Universität Bochum, Germany; T. Hepp, O. Briel, Dockweiler Chemicals GmbH, Germany; A. Muriqi, Tyndall National Institute, University College Cork, Ireland; C. Cho, Ruhr Universität Bochum, Germany; M. Nolan, Tyndall National Institute, University College Cork, Ireland; A. Devi, Leibniz Institute for Solid State and Materials Research, Dresden (IFW), Germany

Scandium oxide (Sc_2O_3) thin films have garnered significant attention in recent years due to their unique properties and versatile applications. The unique combination of high melting point, wide bandgap, high refractive index, and excellent dielectric properties makes scandium oxide an attractive candidate for advanced electronic and optoelectronic devices, such as memory devices, and photodetectors.[1] In particular, the ability of scandium oxide to serve as a high-k dielectric material in thin film transistors (TFT's)[2], highlights the need for versatile low temperature atomic layer deposition (ALD) processes. Although ALD is beneficial to form highly uniform, pure and homogeneous layers of Sc_2O_3 on nanostructured surfaces, there are very few Sc precursors that include the tris-cyclopentadienyl scandium ([$ScCp_3$])[3], substituted tris–R-cyclopentadienyl scandium ([$Sc(RCp)_3$](R=Me,Et,^iPr))[4] and scandium betadiketonates ([$Sc(thd)_3$])[5]. These compounds are associated with certain drawbacks such as low vapor pressure, short shelf life, limited thermal stability and low reactivity. The homoleptic scandium amidinates such as scandium tris-(N,N´-diisopropylacetamidinate)[6] have limited volatility as well.

In our study, we targeted the commercially available new liquid scandium precursor ASGARD [($EtCp_2Sc(dbt)$] (dbt=1,3-bis(1,1-dimethylethyl)-1-triazenato) (Figure 1). Following up on a thorough investigation of the spectroscopical, structural and thermal properties, we adopted a computational approach to evaluate its use in ALD applications. Structure and ligand dissociation energies were calculated and gave a first indication for its suitability as ALD precursor. Furthermore, the interaction towards oxygen and water was investigated, showing its high degree of reactivity. Finally, the promising attributes of this precursor were proven by the development of a water-based ALD process in the temperature range between 220°C and 275°C. Apart from the ALD characteristics like linearity and saturated growth, the high purity of the Sc_2O_3 films could be proven by compositional analysis employing RBS/NRA (Figure 1). These results unveil the favorable characteristics of the new Sc precursor for Sc_2O_3 thin film growth.

2:45pm AF1-TuA-6 Atomic Layer Deposition of Crystalline Molybdenum Trioxide and Suboxide Thin Films, *Alexey Ganzhinov, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Molybdenum oxides (MoO_x) have a range of different oxidation states and crystal structures which affect material properties significantly, leading to a wide range of applications. In addition to the most common stoichiometric molybdenum oxides, such as dioxide (MoO_2) and trioxide (MoO_3), there are multiple nonstoichiometric MoO_x suboxides where x is between 2.75 and 3. Additionally, molybdenum oxides can change oxidation states relatively easily between Mo^{4+}, Mo^{5+}, and Mo^{6+}. This wide range of possible oxidation states and structures allows the control of optical, electrical, and catalytic properties of the material. For example, the resistivity of molybdenum oxide changes from almost metallic for MoO_2 and Mo_4O_{11}, to semiconducting Mo_9O_{26}, and insulating MoO_3. Emerging applications of MoO_x thin films are (organic) semiconductors, organic and perovskite solar cells, catalytic surfaces, and gas sensors.

Due to the plethora of possible different oxides with varying material properties, many new atomic layer deposition (ALD) processes are needed to cover them all. We developed a new ALD process for crystalline MoO_x thin films and deposited first crystalline ALD MoO_x thin films at 200 ℃. Molybdenum acetate dimer ($Mo_2(OAc)_4$) and ozone (O_3) were used as precursors at 200 -– 300 ℃ in a flow type F120 ALD reactor. Films deposited at low temperatures consist purely of unidentified suboxide phase while higher temperatures show α-MoO_3 phase in the GIXRD measurements. The growth rate of the process ranges from ~0.4 Å/cycle at low temperatures to ~3 Å/cycle at 300 ℃.

In-depth composition characterization of the films will be made with X-ray photoelectron spectroscopy (XPS) and time-of-flight elastic recoil detection analysis (TOF-ERDA). Further deposition parameters, such as oxidant type and dose, will be investigated to tune the oxidation state of the thin films from suboxide to trioxide and vice versa during the deposition. Lastly, optical differences between the oxides will be investigated with UV-VIS spectroscopy.

3:00pm AF1-TuA-7 Promising Precursor Chemistry for ALD of Lithium-Based Thin Films, *Jorit Obenlüneschloß,* Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany; *N. Boysen,* Fraunhofer Institute for Microelectronic Circuits and Systems, Duisburg, Germany; *U. Brokmann,* Inorganic Non-metallic Materials, Technische Universität Ilmenau, Ilmenau, Germany; *D. Rogalla,* RUBION, Ruhr University Bochum, Bochum, Germany; *E. Rädlein,* Inorganic Non-metallic Materials, Technische Universität Ilmenau, Ilmenau, Germany; *A. Devi,* Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany

Lithium-containing materials have been particularly difficult to be realized by ALD. This has been mostly attributed to the unavailability of suitable precursor chemistry.[1] That is in stark contrast to the desire to incorporate lithium-containing thin films for battery applications on the large scale.[2] Efforts to utilize oxygen-based precursors such as diketonates (THDs) with low volatility or alkoxides with low thermal stabilities and reactivities are not really promising. Progress has been made with the trimeric lithium hexamethyldisilazane [Li(HMDS)]₃ in the past as a more reactive precursor, but this trimeric compound only provides mild reactivities compared to unstable but highly reactive monomeric Li complexes. Most thin films that have been fabricated via ALD so far were prone to the formation of carbonates, which is often observed for Li containing films.[3]

In our present work we aim at opening pathways to solve the challenges with ALD of lithium containing materials. We propose a highly reactive heteroleptic and monomeric lithium precursor making use of the stabilizing effect of N-heterocyclic carbenes (NHC).

Identifying the stability of monomeric lithium complexes as generally troublesome, we adopted the proven technique of introducing a stabilizing ligand. When employing a NHC with its unique dative abilities due to the free electron pair, electron density can be provided to the electropositive lithium to decrease the strong polarization of the bond between Li and the HMDS ligand. When utilizing NHCs, a monomeric linear Li(I) complex [Li(NHC)(HMDS)] was successfully synthesized. This new complex has been characterized thoroughly by means of NMR, SC-XRD, and LIFDI-MS. Further, it shows excellent thermal properties as evidenced by the TGA (Fig. 1) as desired for ALD.

To prove its utility we set out to develop an ALD process and could successfully fabricate lithium silicate layers when the [Li(NHC)(HMDS)] is reacted with ozone as co-reactant. Self-limiting growth could be confirmed and XPS together with RBS/NRA were employed to prove the presence of both lithium and silicon oxide species, confirming the lithium silicate

material. Making use of the specifically designed precursor, a new and valuable process for lithium-based materials could be realized. The present results set a new pathway in finding highly reactive and yet stable precursor chemistries to deposit Li-containing films by ALD.

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3:15pm AF1-TuA-8 Benchmarking 4 Different Cobalt Precursors for Atomic Layer Deposition of Complex Cobalt Oxides, *Yani Amedjkouh, H. Sønsteby,* University of Oslo, Norway

The world is in an energy crisis. In ICT, the demand for electricity is expected to jump up to 20% of today's production by 2030, mainly due to the rapid expansion of data centers and device networks. The main cause is the inefficiency of modern silicon technology in electronic devices. These devices are so inefficient in fact that 40% of the power use in a typical data center is spent on cooling. Moore's law has held true for over 50 years now but is beginning to fail. Silicon transistors cannot be much smaller than they already are, and therefore we need new materials with new functionalities. Oxides seem to be fit the bill for this purpose, as they host a wide variety of functional properties that have great potential for applications in electronics. The main issue holding these materials back is the lack of viable production methods at an industrial scale. This is where atomic layer deposition comes in. The big chipmakers already use ALD in their production lines, but what's missing are reliable ALD systems for complex oxides for the manufacturers to utilize. To achieve this, research into how different ALD precursors affect the systems is required.

The work we have done aims to serve as a benchmark for four cobalt precursors in a ternary cobalt oxide ALD system. The precursors in question are $Co(acac)_2$, $Co(acac)_3$, $Co(thd)_2$ and $Co(thd)_3$. We have chosen these four as they let us examine the difference between Co(II)- and Co(III)-precursors and the difference between having the larger thd-ligand and the smaller acac-ligand.

We have attempted to grow thin films of both binary cobalt oxide and the ternary $LaCoO_3$ to examine if the difference in precursor affects things as crystallinity, conformity, consistency, and growth rate as these things normally play an important role for the properties of the film material.

We have found that the crystal orientation of binary cobalt oxide deposited on α-Al_2O_3 substrates are affected by the choice of precursor. With the acac-precursors, we observe an additional set of reflections that are not present in films grown with the thd-precursors. Our belief is that the structure relaxes during growth only with the thd-precursors, and therefore we only observe one set of reflections. Furthermore, we have also observed that films grown with $Co(thd)_2$ have a lower growth rate than the rest, but virtually no thickness gradients in the reaction chamber.

It is our belief that the results we find will facilitate the development of novel ALD systems for complex cobalt oxides, as these materials exhibit both electric and magnetic properties.

ALD Fundamentals
Room Hall 3A - Session AF2-TuA

Precursors and Chemistry: Simulation, Modeling, and Machine Learning for ALD

Moderators: Michael Nolan, University College Cork, **Ralf Tonner-Zech**, Leipzig University

4:00pm AF2-TuA-11 Machine Learning Assisted Surface Reaction Study of Al(Me)3 and Water on OH/Si(111), *H. Nakata, Cheol Ho Choi,* Kyungpook National University, Republic of Korea **INVITED**

Knowledge of the detailed mechanism behind the atomic layer deposition (ALD) can greatly facilitate the optimization of the manufacturing process. Computational modeling can potentially foster the understanding; however, the presently available capabilities of the accurate *ab initio* computational techniques preclude their application to modeling surface processes occurring on a long time scale, such as ALD. In this talk, we propose an iterative protocol for optimizing machine learning (ML) training data sets and apply ML-assisted ab initio calculations to model surface reactions occurring during the ALD process on the semiconductor surfaces. The protocol uses a recently developed low-dimensional projection technique, greatly reducing the amount of information required to achieve high accuracy (1 kcal/mol or less) of the developed ML models. Hence, the

proposed protocol furnishes a very effective tool to study complex chemical reaction dynamics at a much-reduced computational cost.

4:30pm AF2-TuA-13 Quantum Chemical Investigation on the Reaction Mechanism of Atomic Layer Deposition of ZrO₂ from Heteroleptic CpZr(N(CH₃)₂)₃ Precursor and Ozone, *Rabi Khanal, R. Joe, A. Dip,* Tokyo Electron America, Inc.

High-k oxides, such as ZrO_2, are being studied as alternatives to SiO_2 due to their advantageous properties for scaling down semiconductor devices. They have lower leakage current, consume less power, switch faster, and are thermally stable. Moreover, they can maintain a high capacitance at thinner film thickness, which is ideal for achieving higher packaging density and increasing memory cell integration on a single chip.

Heteroleptic precursors containing amido and cyclopentadienyl (Cp) ligands exhibit adequate thermal stability for the atomic layer deposition (ALD) of ZrO_2. In ALD, ozone (O_3) can be used as an oxidizer instead of water (H_2O). Ozone has a higher oxidation potential than H_2O. This higher oxidation potential allows for more surface reactions, faster growth, uniform deposition, and reduced impurities. It is worth noting that different ligands in heteroleptic precursors have unique reaction paths depending on their ligand exchange reactions, unlike homoleptic precursors. It is crucial to understand the detailed surface reaction mechanism of ALD to enhance the quality and performance of thin films by reducing impurities incorporated during film growth.

In this study, we have employed quantum chemical calculations at the density functional theory (DFT) level and *ab initio* molecular dynamics (AIMD) to investigate the detailed reaction mechanism of ZrO_2 ALD with the precursor $CpZr(N(CH_3)_2)_3$, and O_3 as an oxidizer. Our findings suggest that when the precursor is adsorbed onto a hydroxylated Si surface, the elimination of the amido ligand is preferred over that of the Cp ligand. During the oxidation process, all remaining ligands on the absorbed precursor are eliminated through the adsorption of O_3 in two subsequent processes, each consisting of multiple intermediate reaction mechanisms.

In addition, the energy barriers associated with the oxidation of Zr-Cp bonds are higher (about 12 kcal/mol) than those of the Zr-N bonds. The higher energy barrier indicates that the release of the Cp ligand occurs after the amido ligand. When the Cp ligand remains on the surface during the ALD cycle, it increases the adsorption energy for incoming molecules and acts as a blocking group to reduce impurity incorporation during film growth. Our study provides a fundamental understanding of the reaction mechanism of various ligands with O_3 at the Si surface, which has yet to be reported. We believe this knowledge can be extended to the deposition of other high-k oxides, such as HfO_2. Also, it can serve as a basis for tuning film properties using feature and reactor scale simulations.

4:45pm AF2-TuA-14 Microkinetic Modelling to Reveal How the Atomic-Scale Mechanism of Deposition or Etch Plays Out at Feature and Reactor Scale, *Simon D. Elliott,* Schrödinger, Ireland*; T. Hughes, T. Ludwig,* Schrödinger*; J. Gavartin,* Schrödinger, UK

Microkinetic modelling is a technique for determining the turnover of a gas-surface process by solving the coupled kinetic rate equations of its constituent elementary reaction steps [1]. It is widely used in the field of heterogeneous catalysis. Here we present a microkinetic model of the atomic layer deposition (ALD) of alumina from trimethylaluminium (TMA) and water and discuss its utility in investigating growth at macroscopic length and time scales.

We first outline the computational scheme, where elementary steps and their activation energies have been computed with density functional theory (DFT), averaging across a wide variety of geometries.We emphasize the importance of converting the DFT energies to free energies at the temperatures and pressures of interest.The resulting microkinetic model for alumina-on-alumina growth yields measurable quantities (relative growth per cycle and sticking coefficients) as a function of temperature and pressure, which are validated against experiment.For instance, the values of sticking coefficient from the model, $s_0(TMA)=7 \times 10^{-3}$ and $s_0(H_2O)= 3 \times 10^{-4}$ at 1 Torr and 300°C, compare well with experiment [2].Sticking coefficients are crucial inputs for computational fluid dynamics simulations at feature-scale and reactor-scale.

We then show results for how microkinetic modelling can be used in specific scenarios.By adding appropriate elementary steps, the model can reveal the contribution from continuous CVD-style growth under given conditions, or under what conditions ALD can be flipped over into ALE.Alternatively, activation energies can be modified to account for the different chemistry that may exist during nucleation on a substrate, without explicitly modelling any one substrate at the atomic scale.This can be used to test which chemistries are effective in tuning area-selectivity of a process towards various substrates.Finally, we show how a microkinetic model can be used to study the variation of sticking coefficient with pressure and thus account for penetration depth and conformality within high aspect ratio features.

These examples illustrate how existing mechanistic data from atomic-scale DFT can be leveraged in computationally-inexpensive higher-scale models to allow 'what-if' experiments to be carried out that link directly to measurements.

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5:00pm AF2-TuA-15 First-Principles Based Comprehensive Surface Kinetic Modeling for Molybdenum ALD Film Growth, *Toshihiko Iwao, K. Lee, J. Cha, J. Hong, J. Son, S. Kang,* Etch/CLN Equipment R&D Team, Samsung Electronics, Republic of Korea

As a design rule of semiconductor device fabrication reaches near tens of angstrom scale, interconnect metallic materials require not only lower bulk resistivity but also smaller electron mean free paths which cause an increase in the effective resistivity of nanometer-scale structures due to interface electron scattering phenomena. Consequently, there is an increasing demand for nanoscale wiring formation using materials with short electron mean free paths, such as molybdenum(Mo), ruthenium (Ru), and cobalt (Co). Among them, the development of Mo micro-wiring formation technology using atomic layer deposition (ALD) is being actively pursued, but further acceleration of productivity is required. In this study we have established a surface reaction model using first-principles analysis to identify the rate-limiting factors of Mo growth mechanism. The construction of reaction models consists of three elements: calculating the activation energy through first-principles surface reaction analysis, determining the reaction pathway, and analyzing real-time coverage using the activation energy.This analysis demonstrates that the temperature dependency of Mo growth-per-cycle (GPC) is caused by the 1.27eV of desorption energy of surface adsorbed hydrogen site Mo-H(s) desorption. During the molybdenum dichloride dioxide (MoO_2Cl_2) precursor dose step, decomposed chlorine and oxygen atoms from the precursor molecule remain on the molybdenum surface and inhibit further precursor molecule adsorption by creating Mo-O-Mo(s), and Mo-Cl(s) surface. This phenomenon describes the monolayer saturated adsorption of the precursor and reveals the necessity of hydrogen flux to remove these inhibitors from the surface. We also analyzed the reaction barrier of removing surface inhibitor by both molecular hydrogen and surface stuck hydrogen site Mo-H(s). By combining these reaction path into surface kinetic model we have successfully reproduced the GPC tendency with over 90% accuracy on various process parameters based on these reaction barrier energy and surface kinetic model, which analyzes the surface coverage in actual process timescale. These film growth analysis scheme provides the detailed and quantitative film growth mechanism for various novel materials and processes.

5:15pm AF2-TuA-16 Modelling the Ligand Exchange Process for the Atomic Layer Deposition of Metal and Metal Oxide Thin Films, *Ji Liu,* Tyndall National Institute, University College Cork, Ireland*; H. Sønsteby,* University of Oslo, Norway*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Atomic layer deposition (ALD) is widely used in microelectronics and semiconductor industry to deposit metal and its oxide and nitride thin films as part of device fabrication in nano- or subnano-dimensions. The key advantages of ALD are the conformality and precise thickness control at the atomic scale, which are difficult for physical or chemical vapor deposition methods. The atomic scale understanding of ALD is vital and essential to design and optimize the deposition process, and density functional theory (DFT) calculations play an important role in providing detailed reaction mechanism, theoretical screening of suitable precursors and estimated growth-per-cycle (GPC).

In this presentation, I discuss our recent work on the detailed first principles simulation of ligand exchange process for thermal ALD of a range of technologically relevant deposition chemistries. 1) Co thin film deposition using $CoCl_2$(TMEDA) and reducing agent Zn(DMP)₂; 2) FeZn thin film deposition using $FeCl_3$ and Zn(Et)₂; and 3) BaO/Ba(OH)₂ using Ba(acac)₂ and oxygen-containing reactants as part of depositing $BaTiO_3$ (BTO). We first focus on gas-phase precursor chemistry and apply DFT calculations to

identify plausible ligand elimination pathways, which allow us to assess the most favourable chemistry for each film deposition. Then we explore the surface chemistry in the two half reactions for the ALD process. For Co deposition we show that a pathway involving initial ligand exchange of DMP and Cl on Co(111) surface with $CoCl_2$ termination and Zn is removed via $ZnCl(DMP)$ formation and desorption, resulting $Co(DMP)_2$ termination on the surface.The two DMP ligands are removed via C-C bond formation in a straightforward way. In intermetallic alloy deposition we show that the $FeCl_3$ precursor is found on the surface as an $FeCl_2$ and -Cl fragment and the reaction with DEZ follows mixture of butane and subsequent EtCl formation and desorption. Finally, for $BaO/Ba(OH)_2$ ALD, we explore how the $Ba(acac)_2$ precursor reacts on Bi-O terminated surfaces and how this can impact on the preferred deposition chemistry. These works showcase how we can apply DFT calculations to elucidate the ligand exchange mechanism during metal or metal oxide thin film growth and give some insights on how the selection of precursors and reducing agent or co-reactant affects the growth behavior.

Atomic Layer Etching
Room Hall 3F - Session ALE1+AM-TuA

ALE & Sustainability

Moderators: Keun Hee Bai, Samsung Electronics Co., **Leila Ghorbani**, KU Leuven and Imec

1:30pm **ALE1+AM-TuA-1** *Sustainable Atomic Layer Processing for Semiconductor Applications, Job Soethoudt,* IMEC, Belgium   **INVITED**
Research into atomic layer processing is key to meeting the growing demand for increasingly complex and versatile semiconductor applications. However, the detrimental adverse sustainability impacts of these semiconductor applications need to be addressed to render them viable for the future. A large part of the life cycle impacts of semiconductor products comes from manufacturing, and recently increasing research efforts are dedicated to making manufacturing more sustainable. The figure below illustrates the CO2-equivalent emissions for production of an integrated circuit, highlighting the contribution of deposition and etch steps. Understanding the source of these contributions can be a catalyst for developing new atomic layer etch and deposition processes with sustainability in mind.

Through data provided within the imec.netzero platform (of which a version is publicly available online) we find that opportunities for sustainable atomic layer processing are as diverse as the field itself, touching on precursor design, reaction kinetics, and surface modification, as well as process engineering and hardware improvements. Moreover, in some cases the unique control offered by atomic layer processing can itself unlock greener IC chip manufacturing methods by unlocking new integration pathways yielding simplified process flows. Together, these opportunities provide new avenues for research to enable a future of sustainable atomic layer deposition and etch processes.

2:00pm **ALE1+AM-TuA-3 Life Cycle Assessment of GaN ALD**, *Houyem Hafdi, A. Carlson, H. Pedersen,* Linköping University, IFM, Sweden
ALD is a fast-growing industry; it is estimated to reach 6,2 Billion USD by 2028, which implies that the demand for metals and energy sources is increasing. Hence, the sustainability of ALD, other nanotechnologies, and nanomaterials has become a major concern and needs to be evaluated[1,2].

Life Cycle Assessment (LCA) is a process for evaluating possible benefits and different environmental impacts through a product´s life cycle based on the defined approaches of ISO 14044[3]and ISO 14040[4]. We will show how to apply the LCA methodology to examine and quantify the sustainability of ALD. We chose GaN as the model material for this study owing our experience of this process and of conventional CVD of GaN, allowing comparisons between conventional CVD and ALD. No research regarding LCA of GaN ALD has been carried out to date.

First, the standard LCA analysis is based on choosing a functional unit, which in our study is the deposition of a 20 nm GaN film from Triethygallium (TEG) and Ammonia (NH3) plasma on a 200nm-diameter silicon substrate. The second step is defining the system boundaries. We chose a cradle-to-gate system that investigates the life cycle phases throughout the entire ALD process. The third step is the inventory analysis where all inputs and outputs are collected, these data include material consumption, electric and thermal energy use, as well as air emissions and by-products. The LCA was carried out based on the Ecoinvent 3 database.

The final step is the impact life cycle assessment, where the results are then transformed into the impact categories of ecotoxicity (ET), global warming potential (GWP), human health (HH), ozone depletion (OD), resource fossil fuels (RFF), human toxicity cancer (HTC), and smog air (SA). We will discuss the sustainability of ALD of GaN from the LCA and pinpoint where the focus should be when making GaN ALD more sustainable.

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2. Pedersen, H., Barry, S. T., & Sundqvist, J. (2021). Green CVD—Toward a sustainable philosophy for thin film deposition by chemical vapor deposition. Journal of Vacuum Science & Technology A, 39(5)
3. ISO 14044; Environmental Management Life Cycle Assessment Requirements and Guidelines. International Standards Organization: Geneva, Switzerland, 2006.
4. ISO 14040; Environmental Management Life Cycle Assessment Principles and Framework. International Standards Organization: Geneva, Switzerland, 2006.

2:15pm **ALE1+AM-TuA-4 Specialization of Atomic Layer Etching to Address Sustainability Challenges**, *Philippe BEZARD,* IMEC, Belgium; *A. Fathzadeh,* KU LEUVEN, Belgium
Atomic Layer Etching (ALE) offers many attractive capabilities such as angstrom-level control over etch depth, excellent anisotropy (with plasma ALE) or isotropy (with thermal ALE), across wafer uniformity, and potentially lower damages than conventional plasma etching. However, in practice, it is rare to find an application where all those capabilities are needed at once and all the time. And thus, pure ALE is rarely found as a main etching process. In terms of sustainability, its extremely low throughput imposes the use of many more etch chambers than conventional processes to reach similar throughput, thereby multiplying consumption of process water, compressed air, power for the entire platform hosting the chambers (pumps, chillers, robots, etc.). Addressing the low throughput of ALE, without considering the type of gas used, is a major improvement for the environment. By only selecting the most relevant etching capabilities for a certain application, better trade-off between patterning performance and throughput can be achieved. Several approaches are tackling this issue such as quasi-ALE, Transient Assisted Plasma Etching, or by using ALE only as a corrective step to a faster sub-optimal etching process.

However, Atomic Layer Etching has several advantages which can be exploited to minimize the consumption of gases hostile to the environment (either by their Global Warming Potential or their toxicity/ corrosivity). First, by allowing enough time for the ions to desorb most etch products, the proportion of etchants adsorbed at the top surface that are used for the formation of a volatile product is high. Second, by removing purges and sacrificing full self-limitation, the outgassing of the reactor walls becomes a major supply of reactants. Cyclic processes such as ALE can be tuned for a better usage of the supplied gas than single-step processes. Finally, provided that enough etchant has been supplied to the entire wafer's surface, the excellent etch uniformity across wafer of ALE allows to run conditions maximizing gas usage which would otherwise be rejected in more conventional processes due to unacceptable compromises in uniformity. These unique properties can be exploited and have profound consequences on the design of the process chamber itself. This family of process should be considered as their own special category (not as a slightly different version of dry-etching), and have its own fully dedicated hardware in order to reduce their environmental impact.

2:30pm **ALE1+AM-TuA-5 Thermal Al_2O_3 Atomic Layer Etching Using HF and Hacac Reactants: Etch Enhancement from Refluorination by Product HF During Hacac Reaction**, *Andrew S. Cavanagh, T. Colleran, A. Abdulagatov, S. George,* University of Colorado at Boulder
Thermal ALE is typically defined by two sequential, reactant exposures separated by a purge. One reactant modifies the surface and the second reactant volatilizes the modified surface layer. In this study, a new ALE reaction process was identified where the surface modification reactant is also a reaction product of the volatilization reaction. Under these circumstances, etching can continue nearly indefinitely by repeating the exposure of the volatilization reactant. This study explores Al_2O_3 ALE using HF as the surface modification reactant and Hacac as the volatilization reactant. The reactions were monitored *in situ* using quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). HF fluorinates the Al_2O_3 surface to AlF_3 in the first reaction and then Hacac volatilizes the AlF_3 surface layer forming $Al(acac)_3$ and HF in the second

reaction. The HF reaction product from the Hacac reaction can then serve as a surface modification reactant to refluorinate the Al_2O_3. By performing multiple mini-doses of Hacac after an initial HF exposure, a large etch rate enhancement is observed for Al_2O_3 ALE compared with a single Hacac mini-dose. Figure 1 displays the QCM response to 10 Hacac mini-doses at 250 °C. Each Hacac mini-dose results in a net mass loss. The first Hacac dose removes the most mass. The 10th Hacac dose removes the least mass. The diminishing returns with subsequent Hacac mini-doses are the result of loss of some HF reaction product to the gas phase. If all the HF were recycled, then the HF reaction product could lead to perpetual etching. Similarly, Figure 2 shows the QMS response for successive Hacac mini-doses on HF-exposed Al_2O_3 at 250 °C. All QMS signals show a diminished response with successive Hacac exposures. The HF^+ signal is evidence of HF produced during the volatilization step that escapes to the gas phase. The H_2O^+ signal is consistent with surface refluorination by HF reaction product. The $Al(acac)_2^+$ and $Al(acac)_3^+$ signals result from volatilization of the AlF_3 surface layer. The diminishing response is attributed to the loss of HF to the gas phase. With ten Hacac mini-doses per cycle, Al_2O_3 etch rates were determined using QCM between 160 – 300 °C. The largest etch rate of 3.07 Å/cycle [91.0 ng/(cm²·cycle)] was observed at 290 °C. The smallest etch rate of 0.04 Å/cycle [1.1 ng/(cm²·cycle)] was measured at 160 °C.

2:45pm ALE1+AM-TuA-6 Elucidating Gas Phase and Surface Reactions of Atomic Layer Etching, *Taylor G. Smith*, University of California, Los Angeles; *E. Crumlin,* Lawrence Berkeley National Laboratory*; J. Chang,* University of California, Los Angeles

Atomic layer etching (ALE) is playing an increasingly important role in the manufacturing of nanoelectronics and other devices. Theoretical calculations are often used to screen for viable ALE processes by predicting thermodynamically favorable etch products. However, experimental verification of the predicted etch products is needed. In this work, magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) and ambient pressure X-ray photoelectron spectroscopy (AP-XPS) are explored as methods to study ALE mechanisms in the gas phase and at the surface.

Recent advances in MAS-NMR rotor design have enabled the study of heterogenous systems, and this work builds on these advances to study the vapor-solid interactions that lead to etching in thermal ALE processes[1]. A novel MAS-NMR rotor packing method is discussed that is adapted specifically to the study of vapor solid interactions that are the backbone of thermal ALE. This method allows for segregation of a liquid etchant from the solid at room temperature, but exposes the solid to vapor phase etchant when the rotor is heated. MAS-NMR is then used to study the thermal ALE mechanisms of a CuO system etched in ^{13}C-enriched formic acid vapor, with the results indicating a dimeric product with antiferromagnetically coupled Cu centers, in agreement with predicted results. AP-XPS, in turn, can be used to look specifically at surfaces during thermal reactions. Again, CuO in formic acid is used as a model system to demonstrate the applicability of this technique.

[1] A. Chamas, L. Qi, H.S. Mehta, J.A. Sears, S.L. Scott, E.D. Walter, D.W. Hoyt, *Magn. Reason. Imag.***56**, 37 (2019).

3:00pm ALE1+AM-TuA-7 Thermal Atomic Layer Etching of Ta with NbCl$_5$ and O$_2$, *Juha Ojala*, M. Chundak, M. Vehkamäki, A. Vihervaara, M. Ritala, University of Helsinki, Finland

The widely used Cu interconnects in integrated circuits require diffusion barriers to prevent the diffusion of Cu into dielectric layers and contamination of Cu by the constituents of the dielectric layers. Materials used for this barrier layer include TiN, TaN and Ta metal. Processing these materials in a controllable manner becomes critical as the interconnects and barrier layers need to shrink to accommodate the smaller feature sizes in future integrated circuits. Atomic layer etching (ALE) is one such controllable method, which can be used to thin deposited layers, selectively etch unmasked areas of films, and to remove unwanted deposits in additive manufacturing methods, e.g., as a corrective step in area-selective deposition.

We present an isotropic ALE process for etching metallic Ta, based on oxidation of the surface layer with O_2 and etching of the resulting oxide with $NbCl_5$. The ALE process was studied using XRR and EDS thickness measurements as well as with XPS studies. The films were characterized before and after etching using XRD, EDS, SEM, and AFM. Effect of the film crystallinity on the etching process was studied in detail, along with oxidation of the films during etching.

Etching was studied at 300–400 °C using Ta films consisting of a mixture of cubic α-Ta and tetragonal β-Ta, as well as films consisting solely of α-Ta. It was found that the β-phase of Ta etches much more readily and is also prone to etching with $NbCl_5$ even without the oxidizer. Etch per cycle (EPC) of at least 2.0 and 4.0 Å was found for etching α-Ta at 300 and 350 °C, respectively. Gas phase etching of Ta_2O_5 and other oxides with $NbCl_5$ was also studied.

Dissolution of oxygen into the Ta films during etching was evident, and even a suboxide phase was observed during prolonged experiments. Otherwise, partially etched films were free of impurities. The mixed phase films showed development of island-like morphology due to the different EPC of the two phases, whereas the α-Ta films etched uniformly and had smooth surfaces. This study shows that thermal ALE of Ta is simple to perform in principle, but the phase composition of the metal can have significant effect on etching characteristics.

3:15pm ALE1+AM-TuA-8 Atomic Layer Etching of Tantalum: Unlocking the Etching Mechanism by in-Vacuo XPS Studies, *Mykhailo Chundak, J. Ojala, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Atomic layer etching (ALE) has emerged as a promising tool/method for nanofabrication technologies, offering the incomparable precision and control in material removal processes. The etching mechanism involves a set of self-limiting surface reactions that achieve the atomic-scale precision, uniform etching and volatilization of the modified surface. The reaction mechanism depends on the varieties of factors like chemical energy, kinetic energy etc. To elucidate the mechanisms of the reactions we used the cluster tool setup in HelsinkiALD laboratory[1]. The tool allows us to study the reactions with surface science techniques in vacuo after interrupting the reactions at each pivotal step giving us new insights about the reaction intermediates and thereby processes occurring at the surface.

Here we present results of the etching process of tantalum metal thin films. Tantalum, renowned for its exceptional corrosion resistance, holds significant importance across various industries, including microelectronics, catalysis, and energy storage. The 40 nm thick Ta films were first deposited via filtered cathodic arc discharge (FCAD) and subsequently subjected to an intricate etching process at 300 °C with $NbCl_5$ and O_2 within the cluster tool. Stoichiometry of the films was studied by X-ray photoelectron spectroscopy (XPS) at each step of the etch process. Initially the tantalum films were subjected to sputtering using Ar^+ ions to effectively remove the oxide layer, ensuring a pristine surface for subsequent reactions. Following this, controlled oxidation with O_2 gas was implemented to form surface oxides on the tantalum films. Finally, the tantalum films were exposed to $NbCl_5$, allowing for the observation of chemical composition changes indicative of the etching process. Notably, the etchant effectively removes the tantalum oxide layers starting from the highest oxidation states until the lower ones resulting in the stoichiometry reminiscent of the surface after sputtering.

Through systematic investigation and analysis, this study provides insights into the complex dynamics of atomic layer etching applied to the Ta thin films. The findings contribute to a better understanding of the ALE processes and valuable insights into precise control of the materials modification for further technological applications.

(1) Nieminen, H.-E.; Chundak, M.; Heikkilä, M. J.; Kärkkäinen, P. R.; Vehkamäki, M.; Putkonen, M.; Ritala, M. In vacuo cluster tool for studying reaction mechanisms in atomic layer deposition and atomic layer etching processes. *Journal of Vacuum Science & Technology A* **2023**, *41* (2). DOI: 10.1116/6.0002312 (acccessed 1/30/2024).

Atomic Layer Etching
Room Hall 3F - Session ALE2+AM-TuA

A.I. for ALD and ALE, and Wet-Chemical ALE

Moderators: Eric Liu, Tokyo Electron America, USA, **Kazunori Shinoda**, Hitachi High-Tech Corporation

4:00pm ALE2+AM-TuA-11 Application of Machine Learning to Atomic-Scale Process Development, *Satoshi Hamaguchi,* Osaka University, Japan
INVITED

For the development of new atomic-scale processing such as atomic layer etching (ALE) and atomic-layer deposition (ALD), efficient selection of precursor gases and other process conditions is desired among a large number of possible combinations of them. Artificial intelligence (AI) and machine learning (ML) techniques are expected to facilitate this selection. In this presentation, after briefly reviewing recent developments in data-driven plasma science [1] for process development and control in general,we discuss a method to predict the sputtering yields/etch rates of

materials by ion impact based on experimental and simulation data of sputtering yields/etch rates. In such predictions, the sputtering yield typically depends on a relatively small number of physical parameters that characterize the surface material and incident ions (such as the masses of the surface material atoms and incident ions). However, the availability of large sputtering yield data is crucial for accurate prediction. Because experimental data for specific material and ion combinations may not be available, physics-based numerical simulations can be used to augment these data. For example, classical molecular dynamics (MD) simulations can be used to provide sputtering yield data but interatomic force-field models for "unfamiliar" materials are often of questionable accuracy. A method to develop ML-based interatomic force-field models is presented with an example of Si etching, and the challenges of such methods for general materials are discussed.

[1] R. Anirudh, et al., "2022 Review of Data-Driven Plasma Science" IEEE Trans. Plasma Sci. 51(7) 1750-1838 (2023).

4:30pm ALE2+AM-TuA-13 Surrogate Models for One-Shot ALD and ALE Process Transfer Across Reactors and High Aspect Ratio Substrates, *Angel Yanguas-Gil, J. Elam,* Argonne National Laboratory

Being able to predict the behavior of ALD or ALE processes when transferred from a lab setting to manufacturing would help accelerate the adoption of ALD and ALE in a wide range of applications, from energy materials to microelectronics. Current approaches require extensive tool time and characterization or, when assisted by simulations, accurate models carefully tuned to each specific process. In addition to reducing the risk and cost of adopting new processes, being able to predict the behavior of a specific precursor across reactors and types of substrates can also be used to discriminate processes that struggle to perform well under more challenging conditions present in manufacturing. A key challenge is our lack of information about many ALD and ALE processes. This includes not only the surface kinetics, but in many cases the precursor pressure in the reactor or upstream precursor consumption. It is therefore key to understand how can we compensate for this lack of information with more readily available experimental data.

In this work, we tackle this problem from a machine learning perspective. In particular, we have focused on using surrogate models as tools to help us understand the following two questions: 1) how can we predict process performance across reactors and substrates?; 2) what are the key experimental observables that we need in order to make such connection? Building on our prior work on artificial neural networks for ALD process optimization,[1] we constructed surrogate models trying to connect experimental data under lab conditions with key process metrics relevant for manufacturing. These include predicting throughput, precursor utilization, process variability across large area substrates, or expected conformality. These models are built using datasets from simulations that have been shown to agree well with experimental data for a few known processes, such as Al_2O_3 growth from trimethylaluminum and water.[2] Our results show that a careful experimental design involving the characterization of film thickness at predefined reactor conditions under undersaturated conditions is often enough to compensate for the lack of knowledge of a specific process. The downside is that the surrogate models are dependent on the specific reactor geometry. However, within a given reactor, surrogate models show predictive behavior across a wide range of surface kinetics and precursor pressures as long as the process kinetics is represented in the training set.

[1] A. Yanguas-Gil and J. W. Elam, *J. Vac. Sci. Technol. A* 40, 062408 (2022)

[2] A. Yanguas-Gil, J. A. Libera and J. W. Elam, *J. Vac. Sci. Technol. A* 39, 062404 (2021)

4:45pm ALE2+AM-TuA-14 Ligand-Assisted Surface Layer Formation in Wet Atomic Layer Etching of Molybdenum, *Tulashi Dahal, K. Abel,* Tokyo Electron America Inc.*; N. Levtchin,* TEL Manufacturing and Engineering of America, Inc.*; T. Hurd,* Tokyo Electron America Inc.*,; A. Rotondaro,* Tokyo Electron America Inc.

There are many applications for molybdenum in the semiconductor industry including metallization in logic BEOL and 3-D NAND. These applications often require partial etch back where the post-etch morphology is critical to device performance. Wet atomic layer etching (ALE) offers materials removal with Angstrom-level precision following two sequential, self-limiting, wet processing steps. In the first step, a Mo surface is exposed to an oxidizing solution that forms a self-limiting oxidation layer.

In the second step, this layer is selectively dissolved in a second solution. Formation of a self-limiting Mo oxidation layer is challenging due to the solubility of molybdenum oxides in aqueous solution, which leads to continuous Mo etch and rougher post-etch morphology. Solubilization of Mo oxides can be delayed in a non-aqueous oxidizing solution. Mo surface oxidation in non-aqueous solution is, however, not self-limiting (Fig. 1). The post-etch morphology of Mo in cyclic etch experiment using non-aqueous oxidizing solution is rougher compared to the starting coupon owing to preferential grain boundary etching. Here we present our results on improving the self-limiting nature of Mo oxidation layer by adding a ligand to the oxidizing solution. Aqueous oxidation of Mo leads to a continuous etch, non-aqueous oxidation leads to a delayed etch, but adding a ligand to the oxidation solution leads to the formation of a stable passivation layer (Fig. 1). Cyclic etch experiments were carried out to estimate the Mo etch rate by exposing the Mo coupon in non-aqueous solution with and without a ligand. The drop in Mo ER from ~0.10 nm/cycle to ~0.07 nm/cycle after adding millimolar amount of ligand in the oxidizing solution indicates the changes in surface chemistry with ligand (Fig. 2). The dissolution of modified layer can be significantly increased via enhanced dissolution kinetics at an elevated temperature nearly doubling the Mo etch rate (~0.12 nm/cycle). Mo ER (~0.12 nm/cycle) is constant from 5 mM to 100 mM of ligand and drops to ~0.08 nm/cycle for higher ligand concentration remaining constant thereafter. The drop in Mo etch rate with higher ligand concentration may be attributed to the piling up of surface products that are less soluble in the dissolution chemistry B. The measured RMS roughness and the SEM images (Fig. 3 and inset) show that addition of a ligand decreases the post-etch surface roughness to the level of the unetched reference coupon. We attribute these differences in etch rate and post-etch morphology to improvements in the conformality and self-limiting nature of the surface oxidation layer with the addition of a ligand.

5:00pm ALE2+AM-TuA-15 Wet Atomic Layer Etching of Ruthenium, *Kate Abel,* Tokyo Electron America, Inc.

We have developed a new process chemistry for atomic layer etching (ALE) of ruthenium (Ru) using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through selective dissolution of a self-limiting passivation layer rather than volatilization. In wet ALE, a self-limiting surface layer is chemically formed upon exposure to the first etching solution. The surface layer must be insoluble in this solution, but readily soluble in the second etching solution in order to complete the ALE cycle. The dissolution of the surface layer in the second solution mayoccur either through intrinsic solubility of the modified layer or through a selective reactive dissolution process. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is therefore required for material removal. A diagram of this process is shown in Figure 1.

Forming a self-limiting layer on Ru that is capable of being selectively solubilized in a second solution is challenging. The common oxides, RuO_2 and RuO_4, are unsuitable – RuO_2 requires harsh, non-selective chemicals to be removed and the low melting point, volatility, and high solubility of RuO_4 prevent the formation of a stable passivation layer. Many non-oxide Ru compounds are known. Synthesis from the metallic state, however, generally requires oxidation to less stable intermediate oxidation states.

In this talk, we show that self-limiting passivation of the Ru surface can be accomplished by controlling both the oxidation potential and co-reactants present in solution. We pair an oxidizer with a variety of co-reactants in solution to show that the chemistry at the Ru surface can be changed from a continuous dissolution process to the formation of a self-limiting surface layer by changing the identity of the co-reactant. In the self-limiting case, completion of the wet ALE cycle can be accomplished through reactive dissolution of the Ru surface layer in a second etching solution. We present quartz crystal microbalance data to show how the oxidation conditions, co-reactant identity, and dissolution conditions influence the behavior of the Ru surface in this cyclic etch process.

5:15pm ALE2+AM-TuA-16 Combined Dry-Wet ALE for Tungsten: A Surface Characterization Study, *Cinzia Chan,* KULeuven, Imec, Italy*; J. de Marneffe,* IMEC, Belgium*; C. Gort,* TU Darmstadt, Germany*; J. Serron, M. Agati,* IMEC, Belgium*; J. Hofmann,* TU Darmstadt, Germany*; S. De Gendt,* KULeuven, Imec, Belgium*; D. van Dorp,* IMEC, Belgium

The continuous device scaling towards atomic-scale dimensions is facing challenges due to increasing complexity at both architecture and structure level. At these scales, the requirements for etching processes are limited to angstrom level. Therefore, atomic layer etching (ALE) and cleaning (ALC) are

currently extensively studied as they utilize self-limiting reactions to etch surfaces with high control.

Tungsten is a material of high interest as it is currently being explored for MRAM and spintronic applications[1,2]. The reported ALE processes are halogen-based plasma[3,4] and often require high temperatures (>200˚C) to form volatile byproducts[5,6]. However, limitations on the thermal budget and the use of plasma processes may be incompatible or detrimental to the exposed materials in the device stack. Therefore, we propose a combined dry-wet ALE approach that consists of a self-limiting oxidation step (dry) combined with a selective oxide removal step in acidic solution. The advantage of a selective wet etch is that it does not induce any physical or structural damage (e.g. amorphization) as compared to a full dry approach.

The proposed dry-wet ALE method was investigated on W blanket layers and patterned structures. Surface oxidation was performed through an O_2 plasma treatment at 60˚C, followed by oxide product removal in dilute HCl solution at RT. Inductively coupled plasma mass spectrometry (ICP-MS) was used to study oxide etching kinetics and selectivity by quantification of the etched surface density of W in time. During the first minutes a rapid removal of W oxide was observed followed by a gradual lowering of the etched surface density towards a constant level that corresponds to the background etch rate of the metal. An oxide/metal etch selectivity of ~100 was found. Selectivity could be further improved by lowering the dissolved O_2 concentration in the etchant. While ICP-MS quantification and TEM inspection revealed that the bulk of the oxide is removed within 20 minutes, post-operando XPS measurements confirmed that a remaining interfacial (sub)oxide monolayer was only removed after 60 minutes of immersion in the acid. Conductive AFM measurements agreed with these observations. The etch per cycle was 0.8nm/cycle while the surface morphology was maintained.

[1] K. Kumar et al., Phys. Rev. Appl., 10, 1, 2021

[2] M. Costa et al., J. Phys. Condens. Matter, 30, 305802, 2018

[3] D. S. Kim et al., Plasma Process. Polym., 16, 9, 2019

[4] K. Shinoda et al., Proc. of SPIE, 10589, 1, 2024

[5] N. R. Johnson et al., ACS Appl. Mater. Interfaces, 9, 34435, 2017

[6] W. Xie et al., J. Vac. Sci. Technol. A Vacuum, Surfaces, Film., 38, 022605, 2020

Emerging Materials
Room Hall 3E - Session EM-TuA

Vapor Phase Infiltration

Moderators: Jolien Dendooven, Ghent University, Belgium, **Sang In Lee**, Synos Foundation

4:00pm **EM-TuA-11 Selective Deposition of Al_2O_3 on Patterned Polymer Substrates using Vapor Phase Infiltration**, *Maggy Harake, Y. Lee,* Stanford University; *B. Yu,* Lawrence Berkeley National Laboratory; *G. D'Acunto,* Stanford University; *R. Ruiz,* Lawrence Berkeley National Laboratory; *S. Bent,* Stanford University

As semiconductor lithography nears sub-10 nm feature sizes with the upcoming adoption of high numerical aperture extreme ultra-violet lithography, patterning materials that enable these small dimensions are not the only challenge. Lithographic materials must facilitate high-precision pattern transfer and ensure uniform feature sizes with minimal placement errors thereby mitigating the stochastic variations that limit density scaling. We have recently introduced a concept of area-selective deposition (ASD) with vapor phase infiltration (VPI) akin to atomic layer deposition, which is a promising tool for high-precision patterning.

Our approach involves utilizing a patterned *two-color* surface modification monolayer, where regions of the *first color* serve as non-growth surfaces resembling conventional ASD schemes, while regions of the *second color* act as growth promoters through enhanced VPI. We engineer the *two-color* surface modification layers by leveraging the versatility and lithographic compatibility of graft-to-polymer brushes.

This work reports on the selective infiltration of Al_2O_3 using VPI on patterned substrates coated with growth-promoting sequence-defined polypeptoid (PP) polymers and polystyrene brushes (PS) (non-growth surface). We investigate PP side-chain chemistry to determine which monomer combinations are most receptive to ALD precursors and gain insight into how to tune the thickness of the oxide film. Furthermore, we consider how three Al precursors (triethylaluminium, trimethylaluminum

(TMA), and dimethyl aluminum isopropoxide (DMAI)), which vary in ligand type and size, interact with and influence growth within the polymers and lead to different oxide film densities.

We confirm successful growth of the oxide film on the PP surface of the substrate using atomic force microscopy (AFM). Additionally, blanket substrates covered with PP or PS polymer brushes show large variations in Al uptake and selectivity, as determined by x-ray photoelectron spectroscopy (XPS) and angle-resolved XPS, depending on the ALD precursor-PP interaction. From XPS we determine that TMA creates a thick oxide film within PP and not in PS. DMAI, the larger molecule of the three and the only one containing an Al-O bond, is shown to not be selective between the two types of polymer brushes. In-vacuo infrared spectroscopy measurements provide mechanistic insight into the reactions with the various precursors. Finally, upon reactive ion etching, we demonstrate successful pattern transfer from the VPI-hardened polymer pattern onto the substrate, providing a bridge for existing patterning technologies to be paired with this selective process.

4:15pm **EM-TuA-12 Sequential Infiltration Synthesis of Al_2O_3 in PMMA and PLA Thin Films: Convergence of Results Across Experimental Data and Theoretical Studies**, *Michele Perego,* CNR-IMM, Agrate unit, Italy; *A. Motta, G. Seguini, C. Wiemer,* CNR-IMM, Agrate Unit, Italy; *K. Ronnby, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Sequential infiltration synthesis (SIS) is a vapor phase infiltration technique for the creation of organic-inorganic hybrid materials and/or inorganic nanostructures from a suitable polymer template. So far, the number of inorganic materials that can be grown by SIS is quite limited. To expand the materials library and widen the application fields, studies on kinetics, diffusivity, reaction energy and mechanism are necessary.

In this work, Al_2O_3 is infiltrated in poly (methyl methacrylate) (PMMA) and poly (lactic acid) (PLA) thin films by means of a standard ALD reactor, operating at 70°C in quasi-static mode, using trimethyl aluminium (TMA) and water. Selected polymers are characterized by the presence of ester groups that are expected to act as reactive sites for TMA. In situ spectroscopic ellipsometry reveals that significant swelling and deswelling of PMMA occur during TMA exposure and purging, respectively, due to sorption and subsequent desorption of TMA molecules that are not stably incorporated into the PMMA matrix. PLA exhibits a much larger swelling than PMMA during TMA exposure, but no significant deswelling is observed during purging, suggesting that a large amount of infiltrated TMA molecules is effectively trapped into the polymer matrix by a stable chemical bond. Accordingly, ex-situ XPS analysis demonstrates that much more Al_2O_3 is grown in PLA than in PMMA. Additionally, ex-situ XPS analysis indicates that, in both cases, TMA incorporation occurs through the formation of an Al-O covalent bond at the C-O-C group, as already observed in other biopolymers.

Two density functional theory (DFT) approaches were used to investigate the infiltration of TMA into PMMA and PLA polymers. Binding configurations and energies were modelled using a gas phase model of a ten-unit polymer. For both polymers, TMA was found to form an adduct with the oxygen in the C=O with an exothermic reaction energy, consistent with experiment. Furthermore, TMA was able to exothermically insert into the C-O-C bond of PLA, forming a covalent Al-O bond, aligning with the ex-situ XPS results. Infiltration modelling employed a periodic model with two eight-unit polymer chains. Both PMMA and PLA displayed swelling upon TMA infiltration, saturating with increasing TMA, consistent with experimental findings.

This combined experimental and theoretical study provides insight into SIS of Al_2O_3 in PMMA and PLA. The methodology can be extended to other precursors or polymers, unravelling of the complexities of SIS at the molecular level.

4:30pm **EM-TuA-13 Expanding the Toolbox of Vapor Phase Infiltration Processes**, *Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel **INVITED**

Vapor phase infiltration (VPI), also named sequential infiltration synthesis (SIS), is a technique derived from ALD that enables the incorporation of inorganic species into polymeric matrices. VPI can modify the properties of polymers by creating hybrid organic-inorganic materials with enhanced mechanical, electrical, optical, or catalytic functionalities. In addition, polymer patterns can be used as templates for confined growth, enabling simple conversation of organic nanostructures into inorganic ones, upon polymer removal. With these abilities, VPI is an appealing technique for a wide range of applications- from nanopatterning and sensing to energy

storage devices and water filtration membranes. To continue expanding VPI processes, key challenges need to be addressed. These include new VPI chemistries, better understanding and control over growth processes and depth gradients, as well as new polymer chemistries, morphologies, and architecture for VPI.

Here I will describe our efforts in addressing these challenges. To expand VPI chemistries, we demonstrated the use of TDMA ligands in VPI, creating SnO_2 and HfO_2 nanostructures from block copolymer templates. Despite the large volume of these precursors that reduce diffusion through the polymer, exploring the parameter space of VPI enabled us to rationally design these processes. We also explored new ways for fabricating multi-material structures via VPI by controlling either the precursors' diffusion or their ratios in a three-precursor process, leading to spatially controlled structures and doped metal oxides. We investigated ZnO nucleation and growth in an array of polymers, setting design rules for this important VPI process. Finally, we demonstrate how this knowledge can be harnessed for a new application- protecting degradable polymers from UV radiation. We show how VPI can enhance the growth of ALD on the polymer surface leading to the synergic effect of high durability of these sensitive polymers under destructive UV radiation.

5:00pm **EM-TuA-15 Organic-Inorganic Hybrid Thermoelectric Materials Through Vapor Phase Infiltration**, *Kristina Ashurbekova,* CIC nanoGUNE, Spain*; M. Naumochkin, H. Reith, K. Nielsch,* Leibniz Institute for Solid State and Materials Research (IFW), Germany*; M. Knez,* CIC nanoGUNE, Spain

The fabrication of a multiplicity of hybrid thermoelectric (TE) materials is limited by the fabrication methodologies and incompatibilities of the involved materials classes. We present a new set of hybrid materials with covalently bound organic/inorganic interfaces by growing Sb_2Te_3, Sb_2Se_3, Bi_2Te_3, Bi_2Se_3 inside the bulk of the semi-conducting polymer Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) by vapor phase infiltration (VPI). In this work, we focus on the p-type Sb_2Te_3-PEDOT:PSS. $SbCl_3$ and $(Me_3Si)_2Te$ were used for the VPI growth of Sb_2Te_3 inside the bulk of the spin-coated polymer. SEM, SIMS and XPS results showed Sb_2Te_3 infiltration throughout the whole 200 nm polymer depth. TEM showed the rhombohedral phase of Sb_2Te_3 grown in the bulk and on top of the polymer. TE characterization of the hybrids over a temperature range of 293–433 $K$was performed with a lab-on-chip ZT test platform which allowed simultaneous characterization of all in-plane parameters of the films, including the electrical conductivity (σ), Seebeck coefficient (S), thermal conductivity (λ_{total}), Hall coefficient R_H, and the thus derived Power Factor (PF) and ZT. TE characterization was performed over several heating-cooling cycles (293–433 K), until equilibrium of the measured parameters was reached. Interestingly, during the first three heating-cooling cycles, the difference in σ between each measurement increased to values of more than 80 S cm^{-1}, changing from semiconducting behavior to metallic. This likely originates from migration and crystallization of the inorganic phase in the polymer that leads to formation of additional conductive paths. The thermal transport behavior supports this idea, showing a delta λ_{total}decrease by 0.3 W m^{-1} $K^{-1}$with thermal cycling. This indicates that the degree of disorder increases through formation of out-of-plane Sb_2Te_3 crystals. Decoupling of σ from $\lambda_{total}$is related to suppression of the lattice λ by enhancing the boundary-scattering events for heat-carrying phonons. At the same time the chemical bonds in Sb_2Te_3-PEDOT:PSS are promoting the direct electronic interaction between the inorganic and organic phases, facilitating electron transport. Finally, a great increase in S to a value of 135 μV K^{-1} at 293 K was achieved, much higher than the intrinsic S of PEDOT:PSS (20 μV K^{-1}). A remarkable PF of 610 μW m^{-1} K^{-2} was obtained at 433 K, corresponding to σ of 250 S cm^{-1}. The results offer new solutions for energy harvesting technologies with high flexibility. *K.A. acknowledges MSCA IF fundings, No:101032113.*

5:15pm **EM-TuA-16 Surprising, Simultaneously Enhanced H_2/CO_2 Selectivity and H_2 Permeability in Polymer Gas Separation Membranes by 1-Cycle Alumina Atomic Layer Deposition: The Effects of Inadvertent Vapor-Phase Infiltration**, *L. Hu,* University at Buffalo*; W. Lee, A. Subramanian,* Stony Brook University*; E. Deng,* University at Buffalo*; K. Kisslinger,* Brookhaven National Laboratory*; S. Fan,* University of Colorado Boulder*; V. Bui,* University at Buffalo*; Y. Ding,* University of Colorado Boulder*; H. Lin,* University at Buffalo*; Chang-Yong Nam,* Brookhaven National Laboratory

For polymer gas separation membranes that typically rely on the molecular sieving effect, an improved selectivity typically accompanies a lowered permeability, thus limiting a simultaneous improvement of the two parameters (i.e., Robeson upper bound). Here, we discover that polybenzimidazole (PBI), one of the leading membrane materials for H_2/CO_2 separation, can exhibit simultaneously increased H_2 permeability and H_2/CO_2 selectivity, surpassing the Robeson upper bound, once treated by simple, low-temperature (85 °C) 1-cycle alumina atomic layer deposition (ALD).[1] We find that the normal 1-cycle alumina ALD (i.e., not using an intentional exposure-mode protocol), comprising 15 msec sequential dosing of trimethylaluminum (TMA) and water with 10 sec intermediate purging, leads to a surprising vapor-phase infiltration (VPI) of alumina into PBI matrix, penetrating over several micrometers deep into the film. The resulting AlO_x-doped PBI hybrid membrane features remarkably increased H_2 permeability by 120% - 270% and H_2/CO_2 selectivity by 30% at 35 - 200 °C, compared to the untreated control. This unusual, simultaneously enhanced H_2 permeability and H_2/CO_2 selectivity were attributed to the disrupted PBI polymer chain packing by the AlO_x infiltration, which was found to be mediated by the reaction between infiltrating TMA and amine groups available in PBI. The suggested mechanism was further supported by the TMA-only-infiltrated PBI membrane that displayed a similarly increased H_2 permeability. Given the simple and fast treatment protocol, this demonstration showcases a facile and scalable way of utilizing ALD and VPI for engineering and improving polymeric membranes important for CO_2 capture and future H_2 economy.

[1]L. Hu et al., "Few-cycle atomic layer deposition to nanoengineer polybenzimidazole for H_2/CO_2 separation", *Chem. Eng. J.* **479**, 147401 (2024)

Nanostructure Synthesis and Fabrication
Room Hall 3E - Session NS-TuA

2D Nanomaterials by ALD (Including Transition Metal Dichalcogenides)

Moderators: Jeffrey W. Elam, Argonne National Laboratory, **Chang-Yong Nam**, Brookhaven National Laboratory

1:30pm **NS-TuA-1 ALD Young Investigator Award Finalist Talk: Combining ALD Infiltration and Pressure-Assisted Sintering for Fabrication of Electrically Conductive Nanocomposites**, *Benjamin Greenberg, K. Anderson, A. Jacobs, A. Cendejas, E. Patterson, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Electrically conductive nanocomposites are critical components of electrocatalytic devices, thermoelectric generators, flexible electronics, and many other existing or envisioned technologies. In a disordered conductor/insulator composite with nanoscale domains, high and stable conductivity is achievable provided that (1) the conductive phase does not oxidize or otherwise degrade, (2) the conductive domains percolate—i.e., form continuous networks that traverse the material, and (3) the conductive channels within the network have sufficient cross-sectional area.

In this work, we explore a nascent nanocomposite fabrication strategy based on ALD infiltration and pressure-assisted sintering of nanoparticle compacts. Specifically, we use ALD with long static precursor doses (>10 min) to deposit Al-doped ZnO inside ~2-mm-thick porous compacts of ceramic (e.g., ZrO_2, SiO_2) nanoparticles with ~100 nm diameter, and then we use environmentally controlled pressure-assisted sintering (EC-PAS)[1] at ~2 GPa and 700–1000 °C to remove residual porosity and form fully dense composites. Each ZnO:Al ALD supercycle consists of 15 diethylzinc/water cycles and 1 trimethylaluminum/water cycle, and the deposition temperature is 160 °C except during diethylzinc doses, during which it is lowered to 120 °C to prevent metallic Zn deposition. In principle, this ALD/sintering approach (1) prevents degradation of the ZnO:Al by sealing off the bulk of the composite from the atmosphere, (2) forms percolating ZnO:Al via complete and conformal ALD infiltration, and (3) allows control over the conductive channel cross-sectional area via the number of ALD cycles. In practice, we indeed observe complete infiltration: scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS) of a representative sample reveals Zn throughout the depth of the composite. Electrical resistivity, however, is surprisingly high: despite deposition of enough ZnO:Al to yield channels with ~7 nm thickness—predicted to enable metallic (band-like) conductivity[2]—the composite resistivity is >10^5 Ω-cm. Employing SEM-EDS, x-ray diffraction (XRD), electrical measurements, and other characterization techniques, we investigate potential causes of this high resistivity, which include dopant deactivation and disruption of conductive channels during sintering. We also explore several routes toward achieving metallic conductivity, including

in situ post-ALD ozone cleaning and optimization of sintering parameters to maintain the doping level and continuity of the ZnO:Al.

1. H. Ryou *et al.*, *ACS Nano* **12**, 3083 (2018). 2. T. Chen *et al.*, *Nat. Mater.* **15**, 299 (2016).

1:45pm NS-TuA-2 ALD on Particulate Materials: A Comprehensive Review of Processes, Support Materials and Applications, *Peter M. Piechulla, M. Chen,* Delft University of Technology, Netherlands*; R. Puurunen,* Aalto University, Finland*; J. van Ommen, A. Goulas,* Delft University of Technology, Netherlands

Through its course of technology development, atomic layer deposition (ALD) has mostly been applied to flat substrates, typically for applications in the semiconductor industry. Albeit, the inherent processing and coating characteristics of ALD, namely its ability to conformally deposit materials in high aspect ratio geometries with sub-nanometer thickness control, are also attractive for the coating of particulate matter. Application areas requiring substances with large specific surface area, such as heterogeneous catalysis, adsorbents and separations, or highly precise thickness control, such as energy conversion and storage (batteries) or pharmaceuticals are strong drivers for research activities in the realm of ALD on particulate materials. Several scientific review articles on aspects of this field have been published, particularly over the last decade; however, the scope of them is mostly limited to either a processing or an applications point of view.

In this contribution, we present a comprehensive review of the developments in the field of ALD on particles, covering approximately 700 articles in a data-driven rather than anecdotal manner. We target an audience of researchers from the conventional ALD domain who wish to extend their scope of activities to particular media, as well as researchers involved in particle technology who consider ALD as a tool to enhance their technical applications (see supplementary PDF for applications already using ALD on particles). Challenges related to the processibility of powders/particles are addressed by the presentation of an overview of the different reactor engineering approaches implemented. Furthermore, the substrate materials (supports) used are systematically categorized and evaluated with respect to their geometric characteristics (shape and size) but also their surface functionalities. Finally, we cover the range of coating materials attainable and the respective processing conditions; in this way, we also address the similarities and deviations of conventional ALD and ALD on particles in terms of growth characteristics. Through exploring the current state of the art, this review aims to provide both inspiration for new applications of ALD, and a starting point for researchers in particle-based technologies in search of ALD processes for any given application.

2:00pm NS-TuA-3 Tuning MoCl$_5$ Self-Etching Effect for Deposition of 2D MoS$_2$ on 300mm Wafer by Thermal ALD, *Angelica Azcatl-Zacatzi, N. Vu, D. Lee, T. Ngo, R. Kanjolia,* Merck KGaA, Darmstadt, Germany

Crystalline 2D MoS$_2$ is a semiconductor material with potential application in the next generation of logic and memory devices. The adoption of MoS$_2$ for future high-volume manufacturing requires the synthesis of high quality and large area 2D material on substrates of interest. The control of MoS$_2$ film properties such as film uniformity, thickness, and crystallinity are critical for this objective. In the literature, reports of large area deposition of 2D materials include deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). [1] Among the proposed chemical systems for ALD, the MoCl$_5$-based process has produced crystalline 2D MoS$_2$ [2,3].

In this work, we investigate the MoCl$_5$ and H$_2$S system to deposit MoS$_2$ by thermal ALD. The effect of the MoCl$_5$ etch component will be discussed. It was found that self-etching of MoCl$_5$ can be tuned by process parameters such as precursor pulse time and deposition temperature. The deposition window for 300mm SiO$_2$/Si wafer substrates will be presented. X-ray fluorescence, Raman spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy were used to characterize the ALD-grown MoS$_2$. The resulting 2D MoS$_2$ films exhibit low surface roughness, high uniformity across the wafer, and high level of crystallinity [Fig. 1]. The demonstration of large area and high quality 2D MoS$_2$ produced by the MoCl$_5$-based process provides a path toward the implementation of ALD processes for deposition of large area 2D MoS$_2$.

[1] Y. Liu and F. Gu, *Nanoscale Adv.*, 2021, 3, 2117.

[2] Y. Huang, et al., *Thin Solid Films*, 2017, 624, 101–105.

[3] Kim, Y., Song, JG., Park, Y. et al., *Scientific Reports*, Vol. 6, 2016, 18754.

2:15pm NS-TuA-4 Low-Temperature ALD of SbO$_x$/Sb$_2$Te$_3$ Multilayers with Boosted Thermoelectric Performance, *J. Yang,* IFW Dresden, Germany*; S. Mukherjee,* Jio Institute, India*; **Sebastian Lehmann**, K. Nielsch,* IFW Dresden, Germany

Nanoscale superlattice (SL) structures have proven to be effective in enhancing the thermoelectric (TE) properties of thin films. Herein, the main phase of antimony telluride (Sb$_2$Te$_3$) thin film with sub-nanometer layers of antimony oxide (SbO$_x$) is synthesized via atomic layer deposition (ALD) at a low temperature of 80 °C. The SL structure is tailored by varying the cycle numbers of Sb$_2$Te$_3$ and SbO$_x$. A remarkable power factor of 520.8 μW m^{-1} K^{-2} is attained at room temperature when the cycle ratio of SbO$_x$ and Sb$_2$Te$_3$ is set at 1:1000 (i.e., SO:ST = 1:1000), corresponding to the highest electrical conductivity of 339.8 S cm^{-1}. The results indicate that at the largest thickness, corresponding to ten ALD cycles, the SbOx layers act as a potential barrier that filters out the low-energy charge carriers from contributing to the overall electrical conductivity. In addition to enhancing the scattering of the mid-to-long-wavelength at the SbO$_x$/Sb$_2$Te$_3$ interface, the presence of the SbO$_x$ sub-layer induces the confinement effect and strain forces in the Sb$_2$Te$_3$ thin film, thereby effectively enhancing the Seebeck coefficient and reducing the thermal conductivity. These findings provide a new perspective on the design of SL-structured TE materials and devices.

2:30pm NS-TuA-5 Enhancing Electrical Properties of 2D WS$_2$ Grown by ABC PE-ALD with Ion Energy Dose Control, *Cindy Lam, E. Kessels, B. Macco,* Eindhoven University of Technology, Netherlands

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are currently on the roadmap of major semiconductor companies as beyond-Si channel material in field-effect transistors (FETs).[1] While 2D TMDCs are typically grown by chemical vapor deposition (CVD), the addition of post-processing steps such as the transfer to specific substrates limits and complicates the overall fabrication process. Accordingly, atomic layer deposition (ALD) is considered a promising method for the direct growth of TMDCs on planar substrates and 3D structures at low temperatures suitable for back-end-of-line (BEOL) processes and its potential for area-selective deposition.[2] However, the mobility of ALD-grown 2D TMDCs substantially falls behind that of CVD-grown 2D TMDCs often due to smaller grain sizes.

In this work, we present that tuning our developed plasma-enhanced ALD (PE-ALD) process which utilizes an inductively coupled Ar plasma (ICP) as an additional C step (AB → ABC) [3],[4] can modify the material properties of WS$_2$ during film growth. The comparison between WS$_2$ films grown using the conventional AB and ABC process showcases a significant decrease of the resistivity by four orders of magnitude from ~10^8 to ~10^4 $\mu\Omega$-cm due to the improvement of the grain morphology (Fig. 1, SI). While the AB WS$_2$ film was too resistive for Hall analysis, the ABC WS$_2$ film exhibited a strong *p*-type character with a Hall mobility μ_H of 0.78 cm^2/Vs, which is only one order of magnitude lower than CVD-grown TMDCs. Our results demonstrate effectively improving the electrical properties of WS$_2$ using the ABC PE-ALD process. Finally, preliminary results on the ion energy $E_{i,flux}$ and ion flux Γ_i as function of various plasma processing conditions such as the Ar plasma pressure p and plasma exposure time t_p during PE-ALD (Fig. 2 and 3, SI) provide insight into how the material properties can be affected and further tailor them to our specific needs by the use of plasma.

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[2] Balasubramanyam, S. *et al. ACS Materials, 2***(5)***, 511-518.* (2020)
[3] Balasubramanyam, S. *et al. ACS Appl. Mater. and Interfaces, 12***(3)**, 3873-3885. (2020)
[4] Mattinen, M. *et al. ACS Appl. Mater. and Interfaces, 15, 35565-35579.* (2023)

2:45pm NS-TuA-6 Impact of ALD Precursor Choice on Nucleation and Growth of Dielectrics on 2D Materials, *A. Shearer, J. Ko, K. Saraswat, E. Pop, **Stacey Bent**,* Stanford University

2D semiconducting materials have received attention for their potential to facilitate further downscaling of microelectronic devices by overcoming the physical shortcomings of silicon. Due to their inherent atomic thinness and lack of surface dangling bonds, 2D materials can be well-controlled by a gate while preserving the carrier mobility, leading to excellent current switching characteristics, even at the scaling limit. However, the lack of dangling bonds and reactive sites on the surface makes it difficult to deposit a gate oxide by ALD, often leading to sparse nucleation and the growth of films that are low density, defective, rough, and filled with pinholes.

In this work, we employ physisorption-assisted ALD processes and study the nucleation and quality of the deposited dielectrics. We deposit Al$_2$O$_3$ on

Tuesday Afternoon, August 6, 2024

monolayer MoS$_2$ using a series of ALD precursors in order to investigate the impact of the ALD precursor on nucleation. The precursors utilized in this study are dimethyl aluminum isopropoxide (DMAI), trimethylaluminum (TMA), triethylaluminum (TEA), and a novel Al$_2$O$_3$ precursor, triisobutylaluminum (TIBA). Using scanning electron microscopy (SEM), we study film nucleation and continuity as a function of ALD precursor, cycle number, and temperature. The results show that the precursor used in the ALD process dramatically impacts coverage and growth. With the best performing precursor, we observe full coverage of MoS$_2$ after just 3 nm of material is deposited. After optimizing the temperature and purge time of each process to maximize nucleation, we fabricate transistor devices in which the deposited Al$_2$O$_3$ serves as a seed layer for high-k HfO$_2$ deposition to create the gate stack. Using x-ray photoelectron spectroscopy (XPS) and electrical testing, we investigate the character of the dielectric/MoS$_2$ interface. While all three alkyl precursors lead to seed layers and dielectrics that produce functioning devices, the devices with the best performance are obtained by the precursor that achieves a more uniform, smoother, and denser film, which we attribute to improved nucleation and growth properties. This improved deposition also permits the most thinning of the seed layer. The devices fabricated using the best precursor and improved dielectric show excellent performance such as good on/off ratios (10^6), small device-to-device variation (ΔV_T < 1 V), and low effective oxide thickness (~1 nm).This work provides useful insights into how ALD precursors can be designed to improve the quality of dielectrics on 2D materials, potentially improving the viability of 2D materials for wide ranging applications.

3:00pm **NS-TuA-7 Noble Metal Nanoparticles Functionalized 2D Transition Metal Dichalcogenides by Atomic Layer Deposition for Enhanced Sensing Properties Toward Amino Acids**, *Jisang Yoo, S. Lee, J. Kim, I. Sohn, S. Jung, H. Kim,* Yonsei University, Korea

Due to their large surface-to-volume ratio and stability in aqueous environments, two-dimensional (2D) transition metal dichalcogenides (TMDCs) have recently emerged as promising candidates for biosensing materials.[1] Among various biomolecules, amino acids (AAs) have been proposed as one of key biomarkers of human body status and diseases.[2] The changes in the physiological levels of AAs in biological fluids (e.g., blood, urine) can be used to determine not only nutritional status, but also specific diseases including cancer and diabetes. Therefore, monitoring and detection of AA profile can be of significant importance in potential early diagnostics. Recently, the possibility of detecting AA molecules through direct charge transfer after adsorption on the TMDC surface has been theoretically investigated. Particularly, noble metal (NM) nanoparticles (NPs), such as Au and Pt, functionalization has been proposed to improve the adsorption of biomolecules including AAs, thereby significantly enhancing the sensing properties.[3,4] However, experimental demonstration of NM NP-functionalized 2D TMDCs for AA sensing is still lacking.

In this study, we aim to develop a biomolecular sensor to detect AAs using Pt NP-functionalized monolayer (ML) WS$_2$ (Pt-WS$_2$) channel. Using chemical vapor deposition process, we synthesized grain boundary(GB)-rich ML WS$_2$, where GBs can serve as active sites for surface functionalization. By facilitating atomic layer deposition (ALD), Pt NPs were selectively functionalized on GBs of WS$_2$. By optimizing the process parameters such as precursor flux, purge time and cycle number, the size and distribution of Pt NPs were controlled precisely. Following the interaction with AA molecules, n-type charge transfer from AA to Pt-WS$_2$ was confirmed by Raman spectroscopy, photoluminescence and X-ray photoelectron spectroscopy. For measuring the sensing properties, Pt-WS$_2$ based biosensors were fabricated through lithography process. Enhanced sensitivity and a lower limit of detection compared to pristine WS---$_2$ were observed. Additionally, concentration-dependent linearity curve was established. Finally, enhanced selectivity towards other interfering biomolecules (e.g. dopamine and uric acid) was demonstrated through comparative measurements. This study could be contributed to both basic and expanded research on early disease diagnosis through biomarker monitoring.

Reference

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ALD Applications
Room Hall 3 - Session AA-TuP

ALD Applications Poster Session

AA-TuP-1 Scalable Fabrication of Catalysts for Proton Exchange Membrane Water Electrolysis, *Peter M. Piechulla, M. Chen,* Delft University of Technology, Netherlands*; M. Kräenbring, F. Özcan, D. Segets,* University of Duisburg-Essen, Germany*; J. van Ommen,* Delft University of Technology, Netherlands

The phenomenal growth in renewable power generation has even further increased research interest in the fields of energy storage and material conversion through electrolysis. A key element in any electrolysis process is a catalyst tailored to the targeted reaction, e.g. platinum group metals (PGMs) for water splitting. Due to the immense scale of the problem, and the cost and scarcity of PGMs, economical use of these materials is imperative. Hence, catalysts are typically dispersed on a support material, e.g., Pt-loaded carbon black (Pt/C) as cathode catalyst in proton exchange membrane water electrolysis (PEMWE). Compared to bulk Pt, a larger fraction of atoms is exposed at the surface, thus leading to a higher catalytic activity per unit weight of Pt. Traditional fabrication methods for Pt/C, such as incipient wet impregnation, allow control over the amount of deposited Pt; however, the morphology and dispersion are very difficult to control with this method.

In this work, we propose an alternative and economically feasible fabrication route for Pt/C catalyst layers based on ALD. We have previously shown that Pt/C can be fabricated via atmospheric pressure ALD on particles in a fluidized bed (FBR-ALD), a method that is readily scalable [1]. In contrast to traditional fabrication methods, we can control the morphology and achieve a finer dispersion of deposited Pt [1, 2], which enables higher catalytic activity at reduced Pt loading. First, we use FBR-ALD to fabricate tailored Pt/C for PEMWE. Second, to establish the relationship between morphology and performance, we characterize the material using (HR)TEM and rotating disk electrode (RDE) measurements. From the latter, we infer the electrochemically active surface area (ECSA) as a relative indicator for performance. However, a full assessment of Pt/C requires testing in real-world applications, which is why we go one step beyond bare catalyst characterization and demonstrate the use of ALD-made Pt/C in lab-scale PEMWE cathodes. In conclusion, we demonstrate, for the first time, the fabrication of Pt/C via atmospheric pressure FBR-ALD, and its performance in PEMWE cathodes.

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AA-TuP-3 Synergetic Effects of Nanoscale ALD-HfO₂ Coatings and Bionic Microstructures for Anti-Adhesive Surgical Electrodes: Improved Cutting Performance, Antibacterial Property, and Biocompatibility, *Jahra Mariam,* Picosun Oy, Finland

Electrosurgery uses electrical energy for the exact expulsion of diseased tissues with concurrent cutting and coagulation capabilities. These days, electrosurgery is the favored strategy for more than 90% of all surgeries because of its advantages, like better control, quicker hemostasis, and reduced patient pain. To meet the strict requirements of modern electrosurgery, it was crucial to develop a feasible approach to improve the overall performance of surgical electrodes including anti-adhesion and heat dissipation. In this work, we studied a coupled electrode with micro/nano hierarchical structures that are the coated surface that was found to have excellent blood antiadhesive properties when heated above a certain temperature. Additional experiments revealed that the use of a coupled electrode had notable benefits in minimizing cutting forces, thermal damage, and the amount of tissue adhesion. As a result, we chose a coupled electrode with micro/nano hierarchical structures that are made by applying nanoscale hafnium dioxide (HfO2) coatings onto bionic microstructures (BMs). The HfO2-coated electrode is superior to other electrodes in reducing the characteristics of cutting force, thermal damage, and tissue adhesion. Moreover, the electrode exhibited excellent antibacterial properties against E. coli and S. aureus, in addition, the non cytotoxic behaviour of HfO2 is verified, which indirectly proves the biocompatibility of the coupled electrode. This multifunctional coupled

electrode is a highly promising candidate for advancing the field of electrosurgery. Its versatility and capabilities make it an indispensable tool for various surgical procedures. With its impressive performance and potential, this electrode is poised to revolutionize the way we approach surgical intervention.

AA-TuP-4 Plasma Enhanced Atomic Layer Deposition of Hafnium Oxide (HfO₂) Thin Films for MIS and MIM Devices, *Pallabi Paul, E. Brusaterra, I. Ostermay, E. Bahat Treidel, F. Brunner, O. Krüger,* Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik (FBH), Germany

Vertical GaN-based devices are gaining significant attention as an alternative to Si and SiC-based counterparts [1]. There is a rising trend in integrating amorphous oxides developed by atomic layer deposition (ALD) method as gate insulator material in such devices, driven by their favorable properties, such as, relatively high permittivity, large band gap and high breakdown electric field [2,3].

Our work focuses on investigating the structural, chemical and electrical properties of HfO_2 layers fabricated by plasma enhance atomic layer deposition (PEALD) on n-type GaN substrates. The HfO_2 films were developed at 250°C by PEALD technology employing the SI 500 PEALD cluster system from SENTECH Instruments GmbH. Tetrakis(dimethylamido)hafnium (TDMAH) and O_2 plasma served as precursors, respectively, resulting in a growth per cycle of about 0.2 nm/cycle along with a very good uniformity over 100 mm diameter. The film properties and phase transition behavior were characterized by scanning electron microscopy, atomic force microscopy, X-ray reflectometry and X-ray photoelectron spectroscopy techniques. Optimized process parameters enabled films with high refractive index, high density, good stoichiometry, and low impurities; which are crucial for their suitability in device applications. Further, the stability and durability of annealed (at 350°C and 500°C) PEALD HfO_2 layers were examined. Presently, we are investigating the capacitance-voltage characteristics of these layers within MIS (metal-insulator-semiconductor) capacitor structures in order to comprehensively understand the interface trap charges and hysteresis behavior. The obtained data will be compared to our previous work using alternative stacks of thermal and PEALD Al_2O_3 layers [4]. Further, the breakdown field strength of HfO_2 films in comparison to Al_2O_3 based layers will be presented using MIM (metal-insulator-metal) devices.

Ongoing experiments on PEALD HfO_2 layers are executed to evaluate the potential enhancement in device performance as compared to Al_2O_3 multilayer stacks. HfO_2 is anticipated to exhibit a lower sub-threshold slope and a larger gate span, resulting in lower gate charge for the same modulation, thus enhancing energetic efficiency; along with broadening the material portfolio available for such applications.

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AA-TuP-5 Improving the Thermoelectric Properties of α-Mgagsb Through Powder Atomic Layer Deposition, *Irene Garcia, A. Bahrami, P. Ying, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

In recent years, Mg-based materials have started rivalling the performance and reliability of commercial Bi_2Te_3 thanks to doping and phase engineering. Through the application of Powder Atomic Layer Deposition (pALD) on thermoelectric powders, it is possible to create heterogeneous interfaces at grain boundaries. This modification alters carrier and phonon scatterings, ultimately enhancing the material's thermoelectric performance. In our study, we investigate the impact of coating α-MgAgSb with Sb_2Te_3 layers using pALD. The results indicate a consistent and linear decrease in total thermal conductivity as the number of coating cycles increases. To the best of our knowledge, this study marks the first report on the use of non-oxide pALD coatings for thermoelectric optimization. Our findings underscore the efficacy of pALD in reducing thermal conductivity, thereby opening up new avenues for future research on the deposition of oxygen-free semiconductors and pure metals at grain boundaries. This innovation holds promise for further advancing the field of thermoelectric materials.

AA-TuP-6 Industrially Scalable Atomic Layer Deposition of Superconducting Thin Films of Tin on Large Area Wafer Substrates with Applied® Picosun® Morpher™, *Shashank Shukla*, A. Ghosh, J. Mariam, S. Datta, S. Muhammad, S. Younis, A. Sood, Applied Materials Inc., Finland

Thin-film TiN is known to have one of the highest kinetic inductances in superconducting materials, which has implications in a wide range of applications – such as high frequency single photon detectors, ultra-sensitive current detectors, hybrid quantum systems and protected qubit devices (1) . We report on the demonstration of Atomic Layer Deposition (ALD) process of thin film TiN, on large area Si wafer format (300 mm) with Applied® Picosun® Morpher™ class of ALD reactors, with the future possibility of industrial scalability of such films. Atomically thin layers of 100nm TiN films were deposited on 300 mm and 200 mm Si wafers at elevated temperatures with a GPC (growth per cycle) of 0.2 Å/cycle, resulting in uniform TiN films with an effective resistivity of ~150 μΩ-cm. 15 nm of TiN test deposition resulted in a film with refractive index of 1.35, and with a 1σ non-uniformity of 1.35%. This demonstrates the quality of films that can be deposited with ALD for large wafer formats and the near-future possibility of batch ALD of films that are critical for advanced technologies like superconductors and quantum computing devices. X-ray diffraction studies are being undertaken to assess the crystallinities and crystal orientations of the films. Further to our studies, these TiN films will be sent for critical temperature resistivity measurements and XPS analysis for surface defects and surface elemental compositions. All these results will be summarized in our poster presentation. (1)Abigail Shearrow, Dave Awschalom, David I Schuster et al., 2018, Appl. Phys. Lett. 113, 21260

AA-TuP-7 High-performance Dichroic Filters by Atomic Layer Deposition for Large-Scale Neutrino Detectors, *Y. Hu,* Raytum Photonics, Inc; *Feng Niu,* S. Lekarz, W. Lu, Raytum Photonics, inc.

High-performance dichroic filters (DFs) are key photon wavelength sorting devices for Cherenkov and scintillation light in water- and scintillator-based neutrino detectors. Future detectors, DUNE and THIEA, require high-performance large-area DFs at a low cost. DFs are traditionally manufactured by various physical vapor deposition (PVD) techniques with many intrinsic drawbacks such as high cost, and poor large size uniformity. Atomic Layer Deposition (ALD) has been well established for precise thickness control, excellent large-area uniformity, super conformity for coatings on complex surfaces, and low growth temperatures, thus provides an excellent solution to manufacturing various bandpass DFs requiring tight specs for multiple dielectric layer coatings and for precise wavelength positioning and steepness on large area flat and curved glass and polymer substrates.

Raytum Photonics is specialized in developing advanced ALD technology for optical applications. In this presentation we will demonstrate that a long pass (LP) edge filter in 360-500nm with a high transmission band ≥ 90% at 400-500nm, and a low transmission in the blocking band < 400nm has been achieved by ALD consisting of 64 dielectric layers on a variety of glass substrates up to 4-inch diameter in size. The cut-on edge around 400nm is sharp with about 10nm broadening. We will further demonstrate that a short pass (SP) DF in 320-500nm with a high transmission band around 85% < 400nm was successfully fabricated all by ALD consisting of 48 dielectric layers on 100mmx77mm B270 glass substrates with excellent uniformity (<1%) and a sharp cut-off edge with around a 10nm broadening. Optical loss mechanisms, light angular performance, and medium dependence for further improvement were investigated and will be presented.

This work presents a cost-effective DF fabrication method by ALD coating technique for large-scale neutrino detectors with a potential path for commercialization. Prototypes of both LP and SP DFs have been demonstrated and an ALD batch process is being developed and DFs are being produced and are scheduled for the detector performance test in liquid argon at Brookhaven National Lab.

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AA-TuP-8 Remarkable Productivity and Performance of Flexible Indium Zinc Oxide Thin Film Transistors through Composition Engineering via Atmospheric Pressure Spatial Atomic Layer Deposition, *Chi-Hoon Lee, K. Yoo, D. Kim, C. Park, J. Park,* Hanyang University, Korea

Indium-zinc oxide (IZO) thin-film transistors (TFTs), a form of amorphous oxide semiconductors (AOSs), are gaining recognition as ideal channel materials in TFTs. Their attributes include a wide band gap, high on-off ratio, excellent electron mobility, and robust thermal and mechanical reliability. The creation of IZO thin films with varying metal cation ratios has been pursued using methods such as thermal evaporation, chemical vapor deposition (CVD), wet solution process, pulsed laser deposition, sputtering, and atomic layer deposition (ALD). ALD has proven effective in managing nanoscale thickness and adjusting the metal cation ratio, but its low deposition rate hinders industrial productivity. To address this, spatial atomic layer deposition (S-ALD) was proposed. S-ALD, capable of operating at atmospheric pressure, spatially separates the precursor and reactant using an inert gas, thus enhancing the deposition rate.

Our research utilized AP S-ALD to investigate the growth of IZO thin films with varying metal cation compositions. We examined how these compositions influenced the physical and chemical properties of the IZO films. Various characterizations were conducted to thoroughly evaluate the films. Physical properties were analyzed through Hall measurements, X-ray diffraction (XRD), and atomic force microscopy (AFM), exploring the electrical properties, crystallinity, and surface roughness. Chemical properties were evaluated using X-ray photoelectron spectroscopy (XPS), confirming the presence of carbon impurities and changes in the oxygen defect ratio.

Our analysis indicated that the characteristics of IZO films significantly influence the performance of IZO TFTs. We found that indium 43 at% IZO films, demonstrating superior TFT mobility (45.7 cm^2/V·s) and reliability (ΔV_{TH} = 0.63 V), were most suitable for use as active layers in TFTs. Moreover, a bending test performed on these films confirmed their mechanical stability. The findings suggest that IZO TFTs developed via AP S-ALD hold promise for future applications in the flexible electronics industry.

AA-TuP-9 Investigation into ALD-CuS$_x$ as a Precatalyst for Electrochemical CO$_2$ Reduction, *M. Suominen,* Aalto University, Finland; *Miia Mäntymäki, M. Mattinen,* University of Helsinki, Finland; *J. Sainio,* Aalto University, Finland; *M. Putkonen,* University of Helsinki, Finland; *T. Kallio,* Aalto University, Finland

Power-to-X concepts make use of excess renewable energy by converting it into valuable chemicals, fuels or heat. One attractive power-to-X concept is the electrochemical reduction of CO_2 to form more valuable chemicals. In this work, we studied the electrochemical reduction of CO_2 in a flow cell with the aim of transforming CO_2 into formate.[1] Gas diffusion electrodes comprising of O_3-modified single-walled carbon nanotubes were coated with CuS_x precatalyst films using ALD. Two different CuS_x processes were studied in this work, using either $Cu(thd)_2$ or $Cu(acac)_2$ as the copper precursor and H_2S as the source of sulfur. $Cu(thd)_2$ depositions were done at 130 °C and $Cu(acac)_2$ depositions at 160 °C. Different electrode configurations and electrolysis conditions were studied and optimized. The best results were obtained using the $Cu(acac)_2$ precursor, which appears to form a copper(I) sulfide based on XPS quantification of Cu and S, and X-ray diffraction experiments.

Optimized electrolysis conditions (0.5 M $KHCO_3$ (aq) at 40 °C, Figure 1) resulted in Faradaic efficiencies for formate formation in the range of 40 to 50%. Other electrolysis products included H_2 and CO in all experiments. Most of the S was lost during the electrolysis experiments. Sulfur leaching has also been reported in previous studies with CuS_x precatalysts formed using other techniques.[2] Our experiments with ALD copper modified electrodes showed that sulfur plays an integral part in the electrolysis process despite apparently leaching out of the precatalyst in the early stages of the reaction. In a comparison experiment, metallic copper films deposited onto the same electrode and used in the same electrolysis conditions resulted in H_2 as the main reduction product, highlighting the importance of sulfur in obtaining significant amounts of formate in the flow cell system.

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AA-TuP-11 *In-Situ* Crystallization of Atomic Layer Deposited TiO$_2$/MoO$_x$ Stack for Metal-Insulator-Metal Capacitor Application, *Chaeyeong Hwang, W. Jeon,* Kyung Hee University, Republic of Korea

Metal-insulator-metal (MIM) structures, such as capacitors in DRAM devices and blocking oxides in NAND flash memory devices, play a crucial role in determining the operational characteristics of various memory semiconductors. To enhance the performance of these devices, securing high capacitance with low leakage current in MIM capacitors is essential [1].

Among the various high dielectric constant (k) materials, TiO_2 is considered the most promising due to its very high dielectric constant of 170 when in a rutile crystalline structure. Additionally, various atomic layer deposition (ALD) processes for TiO_2 thin films have been developed, making TiO_2 a highly promising candidate. However, achieving a rutile crystalline phase in TiO_2 requires the use of electrodes with crystalline similarity, such as Ru or MoO_2, presenting a limitation [2].

Furthermore, the proposed electrodes, Ru and MoO_2, have critical limitations in adapting to actual applications due to severe morphology degradation during subsequent processes. Ru tends to oxidize to RuO_2 or RuO_4 and reduce to Ru easily due to its relatively low reduction-oxidation resistance, resulting in surface morphology degradation [3]. During the formation of MoO_2, a reduction process inevitably leads to agglomeration phenomena that adversely affect MIM capacitor leakage current [4].

Therefore, in this study, we developed an in-situ crystallization of TiO_2/MoO_x to form a rutile-TiO_2/MoO_2 stack for achieving enhanced MIM capacitor characteristics with high capacitance density and low leakage current simultaneously. Various stack structures with varied TiO_2 and MoO_x film thicknesses were examined. By conducting various analyses, it was revealed that the enhancement in the MIM capacitor properties was attributed to the capping layer formed by a portion of the TiO_2 film preventing agglomeration during the reduction process of MoO_x.

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AA-TuP-13 ALD SiO_2 Provides Efficient Ge Surface Passivation with a Tailorable Charge Polarity, *Oskari Leiviskä,* Aalto University, Finland; *H. Liu,* Aalto University, Finland, China; *J. Fung,* Aalto University, Finland, Hong Kong; *J. Isometsä, V. Vähänisi, H. Savin,* Aalto University, Finland

Atomic layer deposited (ALD) thin films have proven to be a highly effective method to reduce electronic recombination losses caused by defects present at the Si surfaces. Likewise, germanium (Ge) surfaces suffer from the same recombination problem and indeed, various ALD-based surface passivation schemes have been tried recently on them as well. The current methods utilize mainly so-called field effect passivation based on the negative fixed charge present in the film, such as aluminum oxide (Al_2O_3). The fixed charge induces an electric field to the vicinity of the substrate surface and thus prevents surface recombination by repelling electrons away from the surface. The negative charge can, however, be detrimental for certain applications. Therefore, there is a motivation to find a material which provides either a positive fixed charge or even better the ability to tailor the charge polarity.

In this work we propose plasma-enhanced atomic layer deposited (PE-ALD) silicon oxide (SiO_2) layers as a positive charge containing material for passivation of Ge surfaces and apply them as further charge tailoring interlayers for Ge/Al_2O_3 interfaces, as was demonstrated previously for Si/Al_2O_3 interfaces. First, we study 10 nm thick PE-ALD SiO_2 films on n-type single-crystalline Ge wafers from which the charge polarity is determined. Next, the impact of PE-ALD SiO_2 layers at Ge/Al_2O_3 interface is studied by varying the SiO_2 interlayer thickness in the range of 1-20 nm. The passivation quality is monitored by measuring the minority carrier lifetime (τ_{eff}) and the thin film charge (Q_{tot}) is determined from contactless capacitance-voltage (C-V) measurement.

The results demonstrate that a bare PE-ALD SiO_2 film provides lifetimes in a similar range (> 1 ms) as previous state-of-the-art Ge surface passivation schemes. Surface recombination is seen to increase when depositing negative corona charge at the surface (i.e. effective neutralization of fixed charge) indicating the formation of positive charge on the Ge/SiO_2 interface. Figure 1 presents both the τ_{eff} and the Q_{tot} obtained with an SiO_2 interlayer with varying nominal thickness at Ge/Al_2O_3 interface. C-V measurements show that ALD SiO_2 interlayers at the Ge/Al_2O_3 interface allow us to tailor the effective charge polarity from negative to positive by gradually increasing the SiO_2 layer thickness from ultrathin to thicker layers. Changes in the interlayer thickness at the Ge/Al_2O_3 interface caused a shift from negative effective charge to positive as the thickness of SiO_2 increased. This also influences the τ_{eff} measured from these samples, implying an altering presence of field-effect passivation.

AA-TuP-14 Optimization of Thin Film Encapsulation Layers by ALD and SALD for Perovskite-Silicon Tandem Solar Cells, *Aubin Parmentier,* D. Coutancier, Institut Photovoltaïque d'Île de France (IPVF), France; *T. Bejat, S. Cros,* Commissariat aux Energies Atomique et Alternatives (CEA) Liten, France; *D. Muñoz-Rojas,* Université Grenoble Alpes, CNRS, Grenoble INP, LMGP, France; *N. Schneider,* Institut Photovoltaïque d'Île de France (IPVF), France

In the context of decarbonization of energy production, new types of photovoltaic solar cells are elaborated to achieve higher power conversion efficiencies at lower manufacturing costs. One particular solution is considered: tandem silicon-perovskite cells, which combine a silicon bottom cell with a perovskite-based top cell that have reached 33.9 % efficiencies [1]. However, those new architectures come with new challenges. Perovskite are sensitive to humidity, which severely limits their long-term stability. One possible solution to protect them from extrinsic degradation and increase their durability is the use of efficient barrier layers, often referred as encapsulation layers. [2].

Thin Film Encapsulation (TFE) is a powerful method to encapsulate solar cells. Among the various thin film deposition method available, Atomic Layer Deposition (ALD) is an attractive technique. Indeed, it enables the deposition of thin films of controlled thickness, uniform, dense [3], with very low pinhole defect densities and at low temperature (< 100 °C to avoid damaging the perovskite top cell [4]).

Indeed, inorganic or hybrid organic-inorganic nanolaminate structures synthesized by ALD are very promising have Water Vapor Transmission Rate (WVTR, the physical quantity used to quantify barrier properties to water vapor diffusion [5]) values up to the order of magnitude of 10^{-6} g.m^{-2}.d^{-1} [6]. They have already been successfully applied to OLED, which have even more demanding requirements than perovskite cells [7]. In addition, encapsulation films must have sufficient mechanical properties to prevent cracks forming in them when subjected to shocks, and especially bending stresses. There are many candidate materials, most of which are metal oxides (to name but a few: 〚TiO〛_2 [8], 〚ZrO〛_2 [9], MgO [10]). They are often combined in nanolaminate structures with their metalcone hybrid counterparts [6], opening up a wide range of possibilities for the synthesis of encapsulating films.

As water permeation measurements are time-consuming, we are developing strategies to more efficiently screen encapsulation solution and take full benefit from ALD advantages (film versatility, atom-level control of thickness). This study proposes the optimization of nanolaminate layers using numerical simulations and helium permeation measurements. The comparative results obtained with helium diffusion are extrapolable to the results that could be obtained with water [11].

Finally, this study compares the benefits and challenges of ALD and SALD (Spatial ALD).[12].

AA-TuP-15 Atomic Layer Deposition of Thermoelectric Al -Doped Zno (Azo) Films on Flexible Ion Track Etched Pet Templates, *Esa Alakoski,* Jamk University of Applied Sciences, Institute of New Industry, Jyväskylä Finland; *S. Kinnunen,* University of Jyväskylä, Department of Physics, Jyväskylä, Finland; *T. Laine,* Jamk University of Applied Sciences, Institute of New Industry, Jyväskylä, Finland; *T. Girish,* Aalto University, Department of Chemistry and Materials Science, Finland; *J. Julin,* University of Jyväskylä, Department of Physics, Jyväskylä, Finland; *M. Karppinen,* Aalto University, Department of Chemistry and Materials Science, Finland

Atomic scale thickness control and superior conformality make ALD the optimal deposition method for preparing nanostructured coatings and in the case of TE materials coatings with tailored thermal and electronic properties [1]. Even more freedom for "the atomic architect" is given by the development of MLD (Molecular Layer Deposition, "The ALD of organic materials") and the ability prepare organic/inorganic hybrid coatings and superlattice structures.[2] With superlattice structures thermal conductivity of a TE thin films can be significantly reduced e.g with ZnO:HQ(Hydroquinone) by a factor of 1/50 [3]. The most promising field of application of thin film TE devices is in wearable electronics, miniaturized biomedical devices and sensors.

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AA-TuP-16 Improvement of Interfacial Properties of ZrO₂/Al₂O₃/TiN Capacitors Grown by Atomic Layer Deposition through Ar Plasma Treatment, *HyeongJun Kim, H. Yang, W. Lee,* Soongsil University, Republic of Korea

The development of next-generation Dynamic Random Access Memory (DRAM) capacitors emphasizes the scaling of devices by employing high-k dielectric materials to achieve high capacitance and low leakage current at a smaller cell size. DRAM capacitor currently utilizes dielectric material of ZrO_2 and Al_2O_3-based multilayers in mass production. This multilayer structure has been used thanks to its high dielectric constant, appropriate bandgap, and excellent leakage current characteristics. However, challenges arise due to the decrease in dielectric thickness, and it is difficult to maintain the physical properties of the thin film itself or to deteriorate properties due to interfacial layers forming between the electrode and the dielectric film.

While significant study on atomic layer deposition (ALD) is underway for excellent high-k oxides such as ZrO_2, chemical-reaction-based deposition processes have been reported to result in the formation of undesired low-permittivity interfacial layers between the electrode and dielectric layer. This persistent issue leads to degradation in the electrical properties of capacitors. To decrease the so-called extrinsic dead layer effect, the bottom electrode should be prevented from the oxidation or the already formed interfacial layer should be reduced again.

In this study, Ar plasma treatment was applied to planar capacitors of ZrO_2/Al_2O_3 dielectric layer and TiN bottom electrode to suppress the interfacial low-k layer (TiOx, TiOxNy) formed between the bottom electrode and the dielectric film. ZrO_2 and Al_2O_3 thin films were deposited through an ALD process at 300ºC with cyclopentadienyl tris(dimethylamino) zirconium and trimethyl aluminum as Zr and Al precursors, respectively. High density (~200 g/m³) O_3 was used as an oxygen source for both ALD process. Au top electrode was deposited through a thermal evaporation process. Consequently, (top) 60 nm Au/ZrO₂/ 4 nm Al₂O₃/100 nm TiN (bottom) structure was fabricated with various thickness of ZrO_2. To investigate the plasma treatment effect on the interface and capacitor property, Ar plasma treatment was conducted before and after the deposition of the ZrO_2 dielectric film at 300°C. Regardless of the plasma sequence, extrinsic dead layer between Al_2O_3 and TiN was removed and interfacial component of equivalent oxide thickness was decreased from 4.0 nm to 2.9 nm. Furthermore, by controlling the time and power of Ar plasma treatment, the feasibility of plasma treatment in three-dimensional structures was investigated. For Ar plasma treatment time of 4 – 10 min and power of 100-200 W, the capacitance was increased by about 38% with negligible variations.

AA-TuP-17 Enhancing Resistive Switching Properties of TiO₂ Thin Films Grown by Atomic Layer Deposition through Pyramid-Structured PDMS Substrate, *Jaejun Lee, K. Lyu, W. Lee,* Soongsil University, Republic of Korea

The Resistive Random Access Memory (RRAM) is a type of non-volatile memory that has garnered significant attention for its potential advancements in the field of electronic storage. Recently, a well-fabricated RRAM device has been adopted as a key memristive artificial synaptic device for neuromorphic computing applications. RRAM operates based on the reversible Resistive Switching (RS) phenomenon, where the resistance state can be switched between Low Resistance State (LRS) and High Resistance State (HRS) through set operations (transitioning from HRS to LRS) and reset operations (transitioning from LRS to HRS). RRAM has advantages such as non-volatility, allowing data preservation even when power is off, low power consumption, and high speed. However, in commonly used flat RRAM, controlling precise RS is challenging due to the random occurrence of Conductive Filaments (CF). This leads to issues with non-uniform RS characteristics, impacting parameters like set/reset voltage and on/off ratio. To address these issues, researchers are exploring methods such as creating a pyramid-structured substrate[1] or inserting electrode materials between insulators[2] to induce the formation of CFs.

In this study, a polydimethylsiloxane (PDMS) polymer substrate with a pyramid structure, rather than a flat substrate such as Si single crystal, was utilized to induce the formation of CFs in specific regions, aiming to enhance the electrical characteristics. The RRAM device was fabricated by sequentially depositing a bottom electrode, insulator, and top electrode onto the PDMS substrate. The device fabrication involved using a thermal evaporator to deposit Au for both the bottom and top electrodes. The insulator was grown by atomic layer deposition (ALD) to ensure the complete coverage of 3D structured bottom electrode to prevent short-circuiting between top and bottom delectrodes. The insulator layer was deposited using Titanium tetraisoporoxide (TTIP) and H_2O to form TiO_2. Through these steps, an RRAM device with an Au/TiO₂/Au/PDMS structure was created.

The fabricated device was characterized by I-V measurements to evaluate stability, set/reset voltage, and resistance, deriving the on/off ratio with respect to the number of RS cycles. The results demonstrated stable set/reset voltages of 3.15±0.36V and -1.44±0.35V, respectively, even after 1000 RS cycles, ensuring a sufficiently high and stable on/off ratio. This presentation discusses the impact of the pyramid structure on resistance change characteristics and proposes a method to enhance RRAM technology.

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AA-TuP-19 Nucleation of Ald Grown Gate Dielectrics on WS₂ Using Low Temperature Oxygen Plasma Pretreatment, *Robert Grubbs, D. Cott, J. Swerts, B. Groven, T. van Pelt, S. Nemeth, P. Morin, C. de la Rosa, G. Kar,* IMEC, Belgium

Due the ever decreasing device size driven by the electronics industry, the future of channel materials for small transistors is heading toward the use of two dimensional transitional metal dichalcogenide (2d TMD) materials. 2d TMDs are beneficial in the short channel regime because of their potential high on-to-off current ratios and because of their potentially high channel mobilities, or conductance, between the source and the drain. Beyond TMD electrical and structural quality, two large challenges exist for the implementation of TMDs into transistors. First is the electrical contact of source and drain metals to the TMD and second is the deposition of a nanometer thin, high quality, high k, defect free dielectric material on top of the TMD to form the critical transistor gate dielectric. To tackle the second challenge, the surface of WS₂ TMD was functionalized with a low temperature remote oxygen plasma which enabled nucleation sites to form on the surface of WS₂ without catastrophic destruction of the long-range order of the WS₂. From these nucleation sites, ALD HfO₂ and Al₂O₃ using TMEAH (tetrakis(methylethylamido)hafnium)/H₂O and TMA (trimethylaluminum)/H₂O at 200C was deposited as the gate dielectric and a 5 nm thin layer with 100% coverage could be achieved at increased oxygen plasma exposures. This WS₂ functionalization / nucleation process was explored by measuring the effects of oxygen exposure and temperature and their resulting effect on the ALD deposited gate dielectric film. The ALD gate dielectric coverage and its effects on the underlying 2D materialwas quantified with AFM, XPS, photoluminescence and Raman spectroscopy. This research has led to a process where multi-layer WS₂ can be functionalized and a high-quality gate dielectric can be successfully deposited on the TMD channel materials.

AA-TuP-21 New Method for Ohmic Metal to Si Contact Formation Utilizing Highly Charged ALD Dielectric, *Lassi Lahtiluoma, O. Setälä, H. Savin, V. Vähänissi,* Aalto University, Finland

Ohmic contacts are typically achieved by increasing the charge carrier concentration under the metal by heavily doping the surface layer of the semiconductor substrate. However, such a heavy doping can cause damage to the semiconductor crystal structure and increase electrical losses via charge carrier recombination. Moreover, the doping processes require the use of high temperatures, which adds process complexity and restricts the use of certain material combinations. Thus, it would be highly beneficial for the entire semiconductor industry if the ohmic contact could be formed without external doping.

Here we propose a novel concept for ohmic metal to semiconductor contact formation. We utilize a specific atomic layer deposited (ALD) dielectric that is known to have a high charge density when deposited on top of semiconductor. A schematic of the concept is depicted in Figure 1. The charge present in the dielectric induces an electric field to the underlying substrate. Depending on the polarity of the charge, electric field pushes one type of carrier to the bulk and attracts the other towards the surface, leading to the formation of either electron or hole rich surface layer similarly to conventional external doping via phosphorus or boron, respectively. We propose that by etching suitable openings into the dielectric and by depositing a metal layer on top, an ohmic metal to silicon contact could be achieved. The dielectric-attracted carriers should drift underneath the openings and enable current flow in the metal-Si interface.

For experimental testing of the proposed concept, we selected Al_2O_3 as the ALD dielectric, Si as the substrate and Al as the metal. To characterize the quality of the formed Al to Si contact, we fabricated transfer length method test structures and carried out I-V measurements on them. An example of the obtained I-V curves is presented in Figure 2. The results reveal that an ohmic contact can be achieved with the proposed structure, and that the contact resistivities can get as low as 1.10 $m\Omega cm^2$, which is comparable to that of conventional heavily doped contacts (1 $m\Omega cm^2$). As the contact resistivity can be supposedly lowered by increasing the Al_2O_3 charge with e.g. different ALD precursors, higher post-deposition anneal temperatures and nanostructuring the substrate surface, the proposed concept might have potential to dethrone heavy doping as the industry standard for achieving low-resistivity ohmic contact.

AA-TuP-23 Atomic Layer Deposition of Titanium-Sulfide Films- a Study of Growth, Crystallinity, and Electric Properties, *Zsófia Baji,* Centre for Energy Research, Hungary

Since the success of graphene, 2D materials have gained tremendous research interest. Layered 2D semiconductors have recently become widely studied materials as they can be applied in nanosized transistors, photodetector LEDs, solar cells, and sensing devices. Due to their atomically smooth surfaces, the built-in trap concentration can be minimal, and therefore more stable and higher performance devices can be fabricated from them. 2D materials with sizable bandgaps, such as transition metal dichalcogenides have been in the focus of research, as they lack the drawback of the absence of an intrinsic band gap in graphene. The advantages of ALD, including the precise thickness and compositional control and the conformal coating of complex geometries, make it attractive for the surface engineering of these devices.

Titanium sulphide (TiS_2) is a transition metal dichalcogenide with a layered structure similar to that of MoS_2: the strong covalent bonding within the atoms of S-Ti-S forms a sheet like arrangement with the Van der Waals forces holding the layered structure together. Electronic properties of TiS_2 are unique, as the Ti atomic sheets surrounded by chalcogen atoms are highly conductive, and the material exhibits semiconducting or semi metallic properties, with arguments in the literature for both options. TiS_2, however, is not only interesting for theoretical considerations, but also very promising for a number of applications: As the interplanar gap opens the possibility of ion intercalation, it can be applied as cathode material in Li, Na, and Mg ion batteries and hydrogen storage. TiS_2 also shows interesting catalytic properties that can be used as counter-electrode in dye sensitized solar cells. The atomic layer deposition of Ti-sulphides has been possible, but the present work explores the use of Ti-isopropoxide combined with H_2S for this purpose and compares its feasibility with the more widespread precursors.

The deposition took place in a Picosun SUNALE™ R-200 type ALD reactor. Hall measurement in the Van der Pauw configuration was used to determine the specific resistivity, the carrier concentration and the mobility of the deposited layers. Scanning electron microscopic images were taken by a LEO 1540 XB system, transmission electron microscopic imaging was performed using a Titan Themis 200 image corrected TEM/STEM microscope. The atomic force microscope in use for the present work was an AIST-NT, SmartSPM 1010 instrument.

AA-TuP-25 Improved Mechanical Integrity of Li-ion Battery Anode Materials Coated with Al_2O_3 by ALD, *Liliana Stan*, X. Zhou, D. Hou, Argonne National Laboratory; H. Xiong, Boise State University; L. Zhu, Purdue University; Y. Liu, Argonne National Laboratory

Group IV elements and their oxides (Si, Ge, Sn, SiO, SnO_2, etc) are considerable candidates as anode materials for high energy Li-ion batteries. They have much higher theoretical capacity than commercial graphite anode. However, these materials often suffer from structure degradation due to large volume change during cycling. To address this issue, different approaches have been explored including nanostructuring, doping, and surface coating. Al_2O_3 coating by ALD is considered a viable approach to improve the mechanical stability of high-capacity anode materials.

In this study, we used operando focused ion beam–scanning electron microscopy (FIB-SEM) to visualize the surface morphology change of Sn μm-sized particle coated by ALD with Al_2O_3 of different thicknesses (3 nm, 10 nm and 30 nm). We lithiated the Sn particles in operando mode and directly observed the morphology evolution in both coated/uncoated particles during cycling. Although the fracture of Al_2O_3 is inevitable, the Al_2O_3 breaks into a few smaller pieces instead of completely pulverization. The patches of Al_2O_3 that cover the surface of Sn particles provide local protection and reduce crack formation at the early stage of volume

expansion. Interestingly, the 3 nm Al_2O_3 coating layer provides better protection than the 10 and 30 nm coating layers. Overall, the Al_2O_3 coating improves the mechanical property of large volume change anode materials and stabilizes their electrochemical cycling performance.

AA-TuP-27 Superior Reproducibility of Forming-Free Memristive Operation in Carbon Doped HfO_x Film, *Minjong Lee,* Y. Hong, J. Kim, D. Le, D. Kim, University of Texas at Dallas; R. Choi, Inha University, Republic of Korea; J. Rohan, G. Yeric, Cerfe Labs; J. Kim, University of Texas at Dallas

Transition metal-oxide (TMO) memristors have received significant attention for advanced memory applications. The new paradigm of forming-free memristor, introducing additional defects, created a pathway for highly reliable and reproducible memristive operation [1]. In this context, C. A. Paz de Araujo et al. reported born-ON memristive characteristics in spin-on carbon-doped NiO films, which is expected to be correlated electron random-access-memory (CeRAM) with forming-free characteristics [2]. While this technique effectively triggers the prototype's operational mechanism, spin-on deposition exhibits notable limitations in fabricating integrated circuits, particularly for 3D architecture.

In this study, we present the development of a prototype born-ON HfOx memristor achieved through atomic layer deposition (ALD). Carbon was introduced into the HfOx film using a super-cycle approach of atomic and molecular layer deposition (ALD and MLD) processes (Fig. 1a). We confirmed that the combination of ALD and MLD processes enables controllable carbon concentration ranging from 0 to 22% and above. Among these, the HfOx memristor with 15% carbon exhibits born-ON memristive operation. Variability was checked for five batches, and each batch consistently exhibited born-ON memristive behavior with consistent low and high resistance states (LRS and HRS) (Fig. 1b). These born-ON characteristics also provide reasonable device-to-device variations with micrometer-scaled device area (Fig. 2a). Interestingly, the IOFF decreases with a smaller device area, whereas the ON current (ION) does not change significantly. This implies that scaling down the device area to the nanoscale for memristive layers could potentially result in a higher ON/OFF current ratio with reduced IOFF. Moreover, this provides clear evidence that IOFF is more likely to homogeneously transport in the HfOx layer. The homogeneous transport for IOFF in HfOx devices can address stochasticity issues associated with the inhomogeneous size and spatial distributions, ensuring reliable operation for device/batch variations [3]. We thus believe that this carbon doped HfOx memristor stands out as a promising candidate for reliable emerging memory applications.

[1] E. Ambrosi et al., IEEE IEDM, 443–446 (2022).
[2] C. A. Paz de Araujo et al., APL Mater. 10, 040904 (2022).
[3] A. Subramanian et al., Adv. Electron. Mater. 8, 2200172 (2022).

AA-TuP-28 Atomic Layer Deposition of Niobium Oxide using (Tert-butylimido)tris(diethylamino)niobium and Anhydrous Hydrogen Peroxide for Ferroelectric Hafnia Applications, *Jin-Hyun Kim,* T. Ford, M. Lee, D. Le, T. Chu, D. Kim, University of Texas at Dallas; M. Benham, J. Spiegelman, RASIRC; S. Kim, Kangwon University; J. Kim, University of Texas at Dallas

The ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) has attracted extensive attention due to its robust ferroelectric properties and compatibility with back-end of line (BEOL) processes. Our previous research successfully demonstrated the fabrication of BEOL-compatible HZO films as thin as 4 nm using anhydrous hydrogen peroxide (H_2O_2) to achieve low operating voltages and high endurance.[1] However, when processed at low temperatures, HZO films face reliability challenges, including fatigue, imprint, and retention. In addition, the reduction in film thickness leads to an increase in leakage current, which poses a serious challenge to further scaling. The drive for device size scaling also affects electrode thickness, which subsequently limits the tensile stress that is critical for promoting the ferroelectric orthorhombic phase formation in HZO films. Several methods have been proposed to further continue the scaling. One of the potential solutions is to dope or insert a thin layer of niobium oxide (Nb_2O_5) in the TiN/HZO/TiN stack. Recent studies have shown that doping HfO_2 with niobium oxide enhances its dielectric constant while suppressing leakage current.[2] In addition, inserting Nb_2O_5 film between the ferroelectric La-doped HZO and TiN electrode improved the ferroelectric response and reliability.[3] Thus, to reduce the leakage current and promote the formation of ferroelectric orthorhombic phase during scaling, strategies such as Nb doping and interface engineering will be explored.

In this study, we will demonstrate the Nb_2O_5 ALD using (tert-butylimido)tris(diethylamino) -niobium (TBTEA-Nb) and HZO ALD process

using TDMA-Hf/TDMA-Zr supercycle, both using anhydrous H_2O_2. We aim to investigate Nb doping and interface modification on the TiN/HZO/TiN stack, with variations in HZO film thickness.The effects of Nb_2O_5 on dielectric constant, leakage current, and polarization changes in ferroelectric HZO capacitors will be quantified using Keithley 4200A-SCS parameter analyzer and Agilent 4284A CV meter. In addition, the crystallization and composition of the films will be verified by grazing incidence X-ray diffraction and X-ray photoemission spectroscopy. The detailed experimental procedure and results will be presented.

[1] Y. Jung et al., ALD/ALE 2022.

[2] C.Y. Bon et al., AIP Advances 10, 115117 (2020).

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AA-TuP-29 Atomic Layer Deposition of Cobalt Phosphide for Efficient Water Splitting, *Haojie Zhang, S. Parkin,* Max Planck Institute of Microstructure Physics, Germany; *R. Wehrspohn,* Institute of Physics, Martin Luther University Halle-Wittenberg, Germany

Transition-metal phosphides (TMP) prepared by atomic layer deposition (ALD) are reported for the first time. Ultrathin Co-P films were deposited by using PH_3 plasma as the phosphorus source and an extra H_2 plasma step to remove excess P in the growing films. The optimized ALD process proceeded by self-limited layer-by-layer growth, and the deposited Co-P films were highly pure and smooth. The Co-P films deposited via ALD exhibited better electrochemical and photoelectrochemical hydrogen evolution reaction (HER) activities than similar Co-P films prepared by the traditional post-phosphorization method. Moreover, the deposition of ultrathin Co-P films on periodic trenches was demonstrated, which highlights the broad and promising potential application of this ALD process for a conformal coating of TMP films on complex three-dimensional (3D) architectures.

AA-TuP-30 SnS₂ Thin Film with in-Situ and Controllable Sb Doping via Atomic Layer Deposition for Optoelectronic Applications, *Dongho Shin, J. Yang,* IFW Dresden, Germany; *A. Bahrami,* IFW Dresden, Iran (Islamic Republic of); *S. Lehmann, K. Nielsch,* IFW Dresden, Germany

SnS₂ thin film with in-situ and controllable Sb doping via atomic layer deposition for optoelectronic application

Abstract:SnS_2 stands out as a highly promising two-dimensional material with significant potential for applications in the field of electronics. Numerous attempts have been undertaken to modulate the physical properties of SnS_2 by doping with various metal ions. Here, we deposited a series of Sb doped SnS_2 via atomic layer deposition (ALD) super-cycle process, and compared its crystallinity, composition, and optical properties to those of pristine SnS_2. We found that the increase in the concentration of Sb is accompanied by a gradual reduction in the Sn and S binding energies. The work function is increased upon Sb doping from 3.98 eV (SnS_2) to 4.79 eV (Sb doped SnS_2 with 9:1 ratio). When integrated into photodetectors, the doped SnS_2 layers showed improved performance, demonstrating increased peak photoresponsivity values from 19.5 A/W to 27.8 A/W at 405 nm, accompanied by an improvement in response speed. These results offer valuable insights into next generation optoelectronic applications based on SnS_2.

AA-TuP-31 Effects of Alkali-Metal Doping on Current Amplification of Titanium Oxide Thin Film Transistors Prepared by Atomic Layer Deposition, *Ryo Miyazawa, H. Suzuki, H. Takeda, M. Miura, B. Ahmmad Arima, F. Hirose,* Graduate School of Science and Engineering, Yamagata University, Japan

Thin-film transistors (TFTs) have been used as pixel-control switching devices, chemical, gas, and ion sensors. Previously, we demonstrated nanometer-thick titanium oxide TFTs (TiO_2-TFTs) as gas and UV sensors where the drain current was drastically changed by contacts with oxygen, dry air, nitrogen, and UV light [1]. In this study, we fabricated extremely surface-sensitive TFTs using titanium-oxide channels with a thickness of 16 nm as alkali metal detect sensors. The fabricated TFTs showed high current amplification in the order of mA due to sodium adsorption. We used aluminum-silicate multiple films as the sodium adsorption layer. It was reported that aluminum-silicate multiple films exhibited adsorption abilities of sodium, potassium, and cesium [2]. Thus, the nano-channel TFTs with the aluminum-silicate was expected to have strong electric conduction modulation by the adsorption of these. In this paper, the TFT was fabricated

and its operation mechanism was discussed by electrical measurements and device simulation.

TiO_2 was deposited on a Si/thermally oxide SiO_2 substrate using atomic layer deposition.The TiO_2 thickness was at 16 nm. The plasma excited humidified argon was used as the oxidizing agent in the ALD. Subsequently, a heat treatment at 500 °C for 30 min in an atmospheric atmosphere was carried out for crystallization. 100 nm thick Ti electrodes were formed by electron-beam evaporation using a metal mask. For the gate electrode, the oxide film was area-selectively removed and In was fabricated. Finally, 10 nm of aluminum-silicate was deposited as an alkali-metal adsorption layer using room temperature atomic layer deposition. In this study, a combination of monolayer of aluminum-silicate and 15 layers of SiO_2 were deposited repeatedly for 10 cycles. Fig. 1 shows the structural diagram of the TFT.

Fig. 2 shows the relation between drain current and alkali-metal chloride concentration. The adsorption was performed by immersion of the sample in NaCl, KCl and CsCl solutions for 30 minutes each, rinsing with deionized water and drying for 3 hours under atmospheric conditions. The drain current decreases at 100 mM and 1 M for NaCl and KCl. With regards to enhanced drain currents in TiO_2-TFTs, it is considered that the alkali-metal suppressed defect levels in the TiO_2 band gap and thus improves the conductivity of TiO_2. T. Singh et al. reported that in mesoporous TiO_2, alkali-metal doping suppressed oxygen vacancies in TiO_2 and enhanced electrical conduction [3]. We believe that the TiO_2-TFT fabricated in this study can be used as alkali-metal sensors and high-mobility switching devices.

AA-TuP-33 Development of Antibacterial Neurostimulation Electrodes via Hierarchical Surface Restructuring and Atomic Layer Deposition, *Shahram Amini,* Pulse Technologies Inc.; *H. Khosla,* Villanova University; *W. Seche,* Pulse Technologies Inc.; *D. Ammerman,* Rowan University; *M. Maniscalco, A. Blagojevic, H. Choi, P. Tavousi,* University of Connecticut; *S. Elyahoodayan,* University of Southern California; *G. Caputo, J. Hettinger,* Rowan University; *S. Shahbazmohamadi,* University of Connecticut; *G. Feng,* Villanova University

Surgical site and post-implantation infections are amongst the most devastating complications after surgical procedures and implantations. Additionally, with the increased use of antibiotics, the threat of antibiotic resistance is significant and is increasingly being recognized as a global problem. Therefore, the need for alternative strategies to eliminate post-implantation infections and reduce antibiotic use has led to the development of medical devices with antibacterial properties. In this work, we introduce a two-step process using femtosecond laser hierarchical surface restructuring and atomic layer deposition for deposition of ultra-thin and ultra-conformal metal oxide thin films for development of electrochemically active antibacterial platinum-iridium electrodes targeted for use in neurostimulation and sensing/recording applications. It will be demonstrated that due to the unprecedented increase in the surface area of the electrodes post-restructuring, the ALD-deposited antibacterial metal oxide thin films on hierarchically restructured electrodes are capable of releasing sufficient antibacterial metal ions to kill Escherichia coli and Staphylococcus aureus, two common types of bacteria responsible for implantation infections.

AA-TuP-35 Stabilization of Ni-YSZ Fuel Electrodes using an ALD-Grown Aluminum Titanate Interlayer, *Katherine Hansen,* Radiation Monitoring Devices; *Z. Feng,* University of Pennsylvania; *H. Bhandari,* Radiation Monitoring Devices; *J. Vohs,* University of Pennsylvania; *R. Hayden,* Radiation Monitoring Devices

The degradation of the fuel electrode in solid oxide electrolysis cells (SOECs) currently limits their large-scale commercial adoption. This degradation is primarily caused by the agglomeration of nickel in the fuel electrode, resulting in irreversible loss of electrochemical performance. To address this challenge, Atomic Layer Deposition (ALD) was utilized to grow an aluminum titanate (ALT, Al_2TiO_5) film as a chemical anchor. This anchor prevents the migration of nickel in the yttria-stabilized zirconia (YSZ) electrode network. During the standard temperature range for manufacturing SOECs, ALT breaks down into aluminum oxide (Al_2O_3) and titanium oxide (TiO_2), which then bond with the nickel particles and YSZ framework respectively to form the anchor. This process prevents nickel from agglomerating and maintains the number of active sites from the initial nickel loading, thus extending the lifespan of SOECs.

In experiments with YSZ button cells, it was demonstrated that an ultrathin ALT interlayer, measuring < 5 nm in thickness, infiltrated into the porous YSZ electrode, significantly improved the thermal stability of the nickel in these cells. This improvement was evident in the cell's electrochemical

performance, shown through current-voltage (IV) polarization curves and Electrochemical Impedance Spectroscopy (EIS), and in reduced migration and agglomeration of nickel, as seen in SEM cross-section images. The study's findings demonstrate that a 2 nm-thick ALT interlayer deposited by ALD does not adversely affect the cell's ohmic resistance and effectively prevents nickel sintering and the loss of active area during high-temperature accelerated stress testing. However, thicker ALT layers, while improving nickel stability, impede oxygen ion transport in the electrode and significantly increase the cell's ohmic resistance of the cell, leading to a decline in performance.The ALD ALT chemical anchor for the fuel electrode in SOECs enhances the long-term stability of SOECs, providing an efficient method of storing excess energy from various low-cost and renewable electricity sources as hydrogen fuel, as well as the reverse in fuel cell mode to produce energy from chemical fuels.

AA-TuP-36 ALD-NiOx Thin Film Growth using Ni(dmb)₂ Precursor for FaPbI₃-based Perovskite Solar Cells, *HYO SIK CHANG*, Chungnam National University, Republic of Korea

Charge transporting materials in perovskite solar cells (PSCs) have played an important role in improving the efficiency. Solution-based spin coatings cause the perovskite to dissolve and degrade the device's stability. Recently, inorganic hole transporting materials (HTMs). such as CuOx, MoOx, and NiOx are used to overcome the disadvantages of organic materials in PSC, such as long-term operational instability, low charge mobility, and incompatible processes. Specifically, NiOx in PSCs exhibits many advantages such as valence band matching with most perovskite absorbers, excellent electron blocking, high transparency, and thermal stability.

In this study, NiO for HTM were grown by atomic layer deposition (ALD) using Ni(dmamb)₂ precursor and H_2O, O_3 oxidants. Physical, electrical, and chemical characteristics such as Ni/O atomic ratio, and NiO conductivity in NiO thin films are being studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), UV-Vis., etc. In addition, we deposited FAPbI₃films using a co-evaporation method, and optimized the film thickness and heat treatment. FAPbI₃ perovskite solar cell using vacuum deposition process shows 15~19 % conversion efficiency. The FaPbI₃ perovskite properties following ALD-NiOx thin film growth will be discussed.

AA-TuP-37 Atomic Layer Deposition of Ultra Low-K Amorphous Boron Nitride for Futuristic Inter Metal Dielectric, *Inkyu Sohn, J. Park, S. Lee, J. Seo, J. Yoo, S. Chung, H. Kim,* Yonsei University, Korea

Scaling down of electronic components encounters a notable obstacle due to the reducing processing speed resulting from increasing RC delays associated with higher resistance and capacitance. Diminishing the dimensions of interconnects, which are metal wires responsible for linking various electronic components on a chip, is essential for achieving device miniaturization and non-conducting (dielectric) layers isolate these interconnects from each other. Until now, the majority of research has concentrated on reducing the resistance of scaled interconnects. This is because integrating dielectrics through low-temperature deposition processes, which are compatible with complementary metal–oxide–semiconductors, presents significant technical challenges. Materials used for interconnect isolation must possess low relative dielectric constants (κ values), act as effective diffusion barriers to prevent the migration of metal into semiconductors, and exhibit thermal, chemical, and mechanical stability. In particular, the International Roadmap for Devices and Systems (IRDS) advocates the advancement of dielectrics with relative dielectric constants (κ values) below 2 by the year 2028. Current low-κ materials, including silicon oxide derivatives, organic compounds, and aerogels, exhibit κ values surpassing 2 and have inadequate thermo-mechanical properties. Recently, Shin et al., have demonstrated ultralow-κ properties of amorphous boron nitride (a-BN) which is deposited by plasma-enhanced chemical vapour deposition (PE-CVD). The synthesized a-BN shows ultralow κ value of 1.15 at operating frequency of 1 Mhz. However, with the paradigm shift of memory from conventional planar structures to 3D architectures such as 3D DRAM or monolithic 3D integrated device, there is a need for atomic layer deposition (ALD) processes that can conformally deposit materials onto the intricate 3D structures. Here we report 4 nm thick a-BN films deposited by plasma enhanced atomic layer deposition (PE-ALD) with ultralow κ values of 1.43 (close to that of air, κ = 1) at operation frequencies of 1 MHz. The growth per cycle (GPC) is confirmed to be ~0.12 Å/cycle at 350 °C and the thickness of synthesized film linearly increased with the number of ALD cycles. The RMS roughness is only 1.23 nm even at 30 nm thick of a-BN which indicates the formation of smooth surface of our ALD process. Also, XPS shows the stoichiometric a-BN and TEM, XRD, Raman confirms the amorphous nature of BN. Our results demonstrate that ALD a-BN process holds the potential for application in the realization of next-generation 3D integrated devices.

AA-TuP-38 Approach to Quantitatively Imaging the Equivalent Oxide Thickness of a High-K Oxide Film on Silicon: A Dc-Free Scanning Capacitance Microscopic Method, *Mao-Nan CHANG*, Department of Physics, NCHU, Taiwan; *C. WANG,* Institute of Nanoscience, NCHU, Taiwan

Scanning capacitance microscopy (SCM) is a well-known and reliable technique for surface electrical analysis, providing electrical images of a nanometric area. For many years, SCM has been an important method to observe and to analyze the carrier distributions and p-n junctions in semiconductor materials and devices. Recently, the signal intensity model for SCM measurements was well-established and used to develop novel applications, such as evaluating equivalent physical thickness and dielectric constant of a thin dielectric piece. The signal intensity model also provides a good opportunity to explore the subtle relation between the SCM signal and the electrical thickness for an oxide film on silicon. In this work, a novel and promising method using dc-free SCM to quantitatively evaluate and image the equivalent oxide thickness (EOT) of a high-k oxide/SiO_2 stacked film on silicon was developed. The sample structure used in this work was a high-k oxide/SiO_2 stacked film on a p-type silicon substrate with an Ohmic back-contact electrode formed by aluminum deposition and thermal annealing. After atomic layer deposition for growing the high-k oxide, thermal annealing at different temperatures was performed in an ambient N_2. A scanning probe microscope system (Bruker Dimension ICON) equipped with an SCM module was used to acquire the differential capacitance signals of the samples. A conductive tip was used to perform dynamic dc stress at sample biases of 3 V, 4 V, and 5 V. Upon the dc stress, a dc-free SCM method was employed to observe the time-dependent variation of equivalent oxide thickness induced by charge-retention loss. Using reliable references, *e.g.*, SiO_2 on Si, a control line showing the linear relation between SCM signal ratio and EOT ratio was obtained in order to convert the differential capacitance signals into EOT values. In other words, one can convert the SCM image into EOT image through image operation. The time-dependent EOT variation indicated that the spontaneous charge de-trapping after dc stress is very limited for high-k oxide/SiO_2 stacked films. In comparison with a thermally-grown SiO_2 film on Si, charge retention in the high-k oxide/SiO_2 stacked film was obvious and kept for a long time after dc stress. Similar phenomena were observed under different dc stress conditions. It is worth to notice that the dc-free SCM method also avoids the impact induced by dc voltages for evaluating the EOT of the high-k oxide/SiO_2 stacked film.

AA-TuP-39 Investigation of Thermal Atomic Layer Deposition for Vertical-Channel IGZO FET with Good Performance and Thermal Stability, *J. Xiang,* Beijing Superstring Academy of Memory Technology, China; *X. Duan,* Institute of Microelectronics of the Chinese Academy of Sciences, China; *X. Ma, P. Yuan, **Yuting Chen,** L. Chai, Z. Jiao, Y. Shen, G. Wang,* Beijing Superstring Academy of Memory Technology, China; *D. Geng,* Institute of Microelectronics of the Chinese Academy of Sciences, China; *C. Zhao,* Beijing Superstring Academy of Memory Technology, China

Emerging computing applications such as ChatGPT and AR/VR are demanding memory chip for larger capacity and lower power consumption. IGZO-based DRAM has attracted considerable attention recently due to the extremely low off-current and BEOL compatibility of IGZO FETs. And vertical channel transistors are a promising approach to realizing 3D DRAM. In this work, we utilized thermal ALD process to deposit IGZO channel for vertical channel FET. By utilizing a fully thermal ALD process during IGZO-channel/GI deposition and applying appropriate gate film stack, the fabricated vertical channel FET exhibits good device performance and thermal stability, which is an excellent result among ALD-IGZO FETs.

AA-TuP-40 Improved Stability of Pt Catalyst for Sustainable Hydrogen Generation, *Mingliang Chen, P. Piechulla,* TU Delft, Netherlands; *M. Kräenbring, F. Özcan, D. Segets,* University of Duisburg-Essen, Germany; *J. van Ommen,* TU Delft, Netherlands

Green hydrogen is gaining increasing attention as a means of transport and energy storage worldwide. The proton exchange membrane water electrolyzer (PEMWE) is one of the promising methods for producing green hydrogen. In PEMWE, platinum group noble metals are commonly utilized to achieve high-efficiency hydrogen production. For example, Pt-loaded carbon black (Pt/C) is typically used as a catalyst at the cathode side, as no other catalysts can currently outperform Pt in hydrogen evolution reaction (HER) [1]. However, as a noble metal, the cost and scarcity of Pt soon

become a bottleneck when scaling up hydrogen production to relevant outputs to partially replace, e.g. fossil fuels.

One potential solution for the economical use of Pt is to minimize its loading in PEMWE while maintaining the performance of the cell. To maximize the utilization efficiency of Pt, better control of the morphology and dispersion of the catalyst should be ensured. Therefore, Pt/C has been synthesized with atomic layer deposition (ALD) to achieve lower loading and enhanced catalytic performance with smaller and more uniform particle sizes as compared to those produced by conventional incipient wet impregnation. However, low Pt loading entails new challenges regarding the long-term stability of the catalyst [2]. In this work, the loading and particle size of Pt are first controlled by ALD. Afterwards, a thin layer of protective material (for example, SiO2) is coated on the outer surface of Pt or the carbon substrate to enhance its stability. Finally, accelerating stability testing of those catalysts was performed in a laboratory PEMWE setup. We demonstrate that by carefully selecting the thickness of the layer and the materials used for the protective coating can be ensured that the intrinsic activity of Pt is not compromised, while strongly increasing the stability.

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[2] Yu, Haoran, et al. "Microscopic insights on the degradation of a PEM water electrolyzer with ultra-low catalyst loading." Applied Catalysis B: Environmental 260 (2020): 118194.

AA-TuP-41 Atomic Layer Deposition of Palladium Nanoparticles for Catalytic Applications, *B. Bawab, R. Zazpe, J. Rodriguez-Pereira, **Jan M. Macak**, University of Pardubice, Czechia*

Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance for various catalytic applications [1]. Due to their scarcity, efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique to facilitate lowering of loading mass on a support of interest [2,3]. Furthermore, ALD is the most suitable technology that can decorate high aspect ratio and high surface area substrate architectures [4]. Due to the governing surface energy variations between noble metals and support surfaces, the growth initiates as nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. The surface energy variations are also known to increase the nucleation delay of noble metals including Pd. In this regard our efforts were laid to improve the functionality with pretreatments on carbonaceous supports which were shown promising to reduce the nucleation delay of ALD deposited Pd.

For electrocatalytic applications, it is important to choose the right substrates. Among the available ones, carbon papers (CP) and titania nanotube (TNT) layers are best choices considering their physio-chemical properties, availability, vast literature, and low costs incurred using these as support substrates in electrocatalysis and photocatalysis. Several surface modifications for CP's and variations on morphological aspects of TNT layers had attracted a great attention form applied fields due to their improved surface area, conductivity, and stability [5-8]. Uniformly decorating these CP's and TNT layers by NPs of catalysts proved to be highly efficient with no boundaries on applications, as shown in our recent papers [9-10].

The presentation will introduce and describe the synthesis of Palladium NPs by ALD on CP substrates [9] and TNT layers with high aspect ratios [10]. It will also includethe corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

AA-TuP-43 Optimizing Izo Tft Performance Through Al Doping Cycle Control via Atmospheric Pressure Spatial Atomic Layer Deposition, *K. Yoo, D. Kim, C. Lee, D. Kim, **Chang-Kyun Park**, J. Park, Hanyang University, Korea*

Oxide semiconductors exhibit excellent electrical properties and thickness uniformity in the amorphous state, and notably low leakage currents, making them desirable materials. Among the notable materials in this category is indium gallium zinc oxide (IGZO), introduced by Hosono Group. In IGZO, indium aids carrier generation, gallium suppresses carriers, and zinc helps in network connectivity between materials. Deposition methods for obtaining such oxide semiconductors include sputtering and atomic layer deposition (ALD). While sputtering offers high productivity, it lacks precise control over ion composition and often requires complex equipment setups with multiple targets. Additionally, it faces challenges in achieving uniformity in large-area deposition and coating thickness. On the other hand, ALD enables precise control over ion composition and ensures excellent thickness uniformity even in complex, high aspect ratio structures.

However, ALD still suffers from low productivity due to its inherent purge time. Spatial ALD (S-ALD) has emerged as a promising approach that retains the advantages of conventional ALD while improving productivity and enabling applications in flexible displays [1,2].

In this study, we employed Atmospheric Pressure Spatial ALD (AP S-ALD) to investigate the effects of substituting gallium ions with cost-effective aluminum ions in IGZO, aiming to enhance productivity in the display industry and secure competitiveness in the flexible electronics market. as shown in **Fig 1**, By utilizing AP S-ALD, we established a window for ALD deposition of In_2O_3, ZnO, and Al_2O_3 films with higher productivity compared to conventional ALD methods. Focusing on IGZO TFTs, we divided the deposition process into different cycles of aluminum incorporation (0, 1, 2, 3 cycles) and examined the electrical characteristics of the films, as shown in **Fig 2**. We observed a decrease in carrier concentration with increasing aluminum cycles, leading to a positive shift in threshold voltage (V_{TH}) and a decrease in mobility, indicating a direct correlation with carrier variation, as shown in **Fig 3**. Optimal reliability was achieved in the region where oxygen vacancies were minimized with increasing aluminum cycles, demonstrated by successful bending tests under conditions mimicking a 1 mm radius for 50,000 cycles in **Fig 4**. Through this study, we validate a method to enhance productivity in flexible display manufacturing by optimizing deposition techniques and incorporating cost-effective ion substitutions.

AA-TuP-44 Effect of One ZrO_2/HfO_2 Thickness of ZrO_2/HfO_2 (Zr/Hf=1/1) Laminate on Characteristics for Non-volatile DRAM, *Tomomi Sawada, T. Nabatame, National Institute for Materials Science, Japan; T. Onaya, The University of Tokyo, Japan; H. Miura, M. Miyamoto, K. Tsukagoshi, National Institute for Materials Science, Japan*

Ferroelectric Zr-doped HfO_2 (HZO) film has been widely investigated as capacitor insulator for future non-volatile DRAM [1,2]. HZO film was generally fabricated from ZrO_2/HfO_2 laminate film, and the Zr/Hf ratio of the ZrO_2/HfO_2 film was controlled by changing the numbers of ZrO_2 and HfO_2 cycle during ALD. However, the influence of thickness of one ZrO_2/HfO_2 layer in the ZrO_2/HfO_2 laminate with the same Zr/Hf ratio on characteristics are not currently understood. In this study, we investigated characteristics of TiN/HZO (ZrO_2/HfO_2 =1/1)/TiN capacitors with various thicknesses of one ZrO_2/HfO_2 layer.

TiN/HZO/TiN capacitor was fabricated as follows: A 10-nm thick ZrO_2/HfO_2 laminate film was deposited on p^+Si/TiN substrates via ALD at 300°C using tris(dimethylamino) cyclopentadienyl zirconium and hafnium precursors and H_2O gases. The thickness of one ZrO_2/HfO_2 layer was varied to 0.098, 0.20, 0.29, and 0.39nm by changing ALD cycles of 1/1, 2/2, 3/3, and 4/4. TiN top electrode was deposited on the ZrO_2/HfO_2 film. Finally, post-metallization annealing (PMA) was carried out at 300, 400, and 500°C in N_2.

All as-grown ZrO_2/HfO_2 films had an amorphous structure. The ZrO_2/HfO_2 films started crystallizing at 400°C when the thickness of one ZrO_2/HfO_2 layer became ≥0.20nm. The crystal structure was mixture of cubic/tetragonal/orthorhombic (C/T/O) and monoclinic phases. On the other hand, we found that the ZrO_2/HfO_2 film with one ZrO_2/HfO_2 layer (0.098nm) remained an amorphous structure at 400°C and started crystallizing at 500°C.

C-V measurements of capacitor was performed at a sweep voltage of ±0.5V and a 10kHz. The dielectric constant (*k*) value was estimated from capacitance at 0V before polarization. The *k* values of all as-grown and PMA300°C capacitors exhibited about 20 regardless of the thickness of one ZrO_2/HfO_2 layer. The PMA400°C capacitors with one ZrO_2/HfO_2 layer (≥0.20nm) exhibited larger *k* values of about 27 compared to that (*k*=20) of the one ZrO_2/HfO_2 layer (0.098nm). Furthermore, the *k* values of the one ZrO_2/HfO_2 layer (≥0.20nm) increased up to 32-35 at PMA500°C. The ferroelectricity was observed at PMA above 400 and 500°C for one ZrO_2/HfO_2 layer (≥0.20nm) and (0.098nm), respectively, according to C/T/O structure as explained. All PMA500°C capacitors exhibited superior breakdown electric field of above 3.0MVcm^{-1} at J=10^{-2}Acm^{-2}.

We concluded that low temperature crystallization and large *k* value can be obtained when the thickness of one ZrO_2/HfO_2 layer become ^{3}0.20nm in the ZrO_2/HfO_2 laminate film.

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AA-TuP-45 Plasma-enhanced Atomic Layer Deposition of Niobium Carbide using a New Nb Precursor and H_2 Plasma and its Application to Diffusion Barrier for Cu and Ru Interconnects, *Chaehyun Park*, M. Kweon, S. Kim, S. Kim, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Nb-based compounds including NbC_x, and NbN_x show a unique combination of properties, such as high melting temperature, good chemical stability, excellent electrical properties, and low resistivity [1] [2]. Due to these outstanding characteristics, Nb-based compounds have been researched for various applications, including hard surface coatings, superconducting devices, gate electrodes and copper interconnect diffusion barrier in semiconductor devices [1]. Thin films of Nb-based materials have been deposited by a variety of techniques, such as physical vapor deposition (PVD), and chemical vapor deposition (CVD). But this method is not expected to be adequate for use in future microelectronic devices which has narrow features with high aspect ratio. Therefore, achieving precise thickness deposition in complex and narrow 3D structures has become increasingly challenging. In this respect, atomic layer deposition (ALD) emerges as the optimal method for fabricating Nb-containing thin films with potential applicability in future technologies. In this study, ALD processes using the new liquid cyclopentadienyl-based Nb precursor, and various reactants such as H_2, NH_3 molecules, and its plasma were reported. Preliminary results indicate that, Figure 1, among these reactants ALD-NbC_x and NbN_x can be controllably deposited using H_2 plasma and NH_3 plasma as a reactant. As a result, we were able to create carbides (ca. 6 % nitrogen) and nitrides (ca. 3 % carbon) through ALD processes. Further experiments were done mainly using H_2 plasma to deposit NbC_x due to its better properties than NbN_x. The NbC_x thin films were grown at the temperature of 350 °C by shower head type PE-ALD reactor (IOV dX1 PEALD, ISAC RESEARCH, Korea). The self-limiting growth behavior was shown with both precursor pulsing and reactant pulsing and the saturated growth rate was approximately 0.19 Å/cycle. Film composition varied with deposition conditions and was characterized by 4-point probe (resistivity), SEM (thickness), TEM (step coverage and thickness), XRR (density and thickness), XRD (crystallinity), XPS (composition) and RBS (impurity) etc. We applied the ALD-NbC_x films to a diffusion barrier for Cu and Ru interconnects as well as gate electrodes and the results will be presented at the conference.

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AA-TuP-46 Ultrahigh Plasma Resistance of Y_2O_3 Thin Films Prepared by Atomic Layer Deposition for Uniform 3D Coatings, *J. Jeon, H. Kim, S. Jang, H. Kim*, Korea Electronics Technology Institute (KETI), Republic of Korea; *C. Park, Y. Lee*, KoMiCo Ltd., Republic of Korea; *G. Yeom, J. Choi*, Sungkyunkwan University (SKKU), Republic of Korea; *Sun Gil Kim, S. Kim, H. Kim*, Korea Electronics Technology Institute (KETI), Republic of Korea

As memory and logic devices are dramatically scaled down, the importance of etch processes for semiconductor manufacturing has been highlightened. To achieve the etch uniformity and selectivity of sub-nanometers patterns with high aspect ratios, the plasma density in etch chambers increases and the composition of plasma gas is becoming more diverse. As a result of exposure to these plasma etching conditions, the inner parts which compose the etch chamber are attacked, resulting in fatal particle contamination on wafers. Therefore, it is necessary to research etch chamber coating materials which have remarkable plasma resistance to attain high production yield by minimizing particle sources. Among ceramic coating materials, yttrium oxide (Y_2O_3) has been highlightened as a material replacing conventional Al_2O_3 coatings since it exhibits outstanding plasma resistance. Also, it is important to fabricate highly dense films with standout step coverage to apply for the delicate 3D parts coatings. Atomic layer deposition (ALD) emerges as a promising technology for the chamber parts coatings due to its self-limiting deposition characteristics, enabling uniform and high density film deposition on complex 3D structures. This study introduces ALD method of Y_2O_3 films, employing a novel yttrium precursor (ARYA™ supplied by AirLiquide) and three reactants (H_2O, O_3, and O_2 plasma). It is confirmed that Y_2O_3 films were successfully deposited without impurities using the ALD process through X-ray photoelectron spectroscopy(XPS) analysis. Furthermore, the crystalline structure and characteristics of the Y_2O_3 films were investigated by X-ray diffraction(XRD) and high-resolution transmission electron microscope(TEM) analysis

depending on the reactants. Also, plasma resistance of the ALD Y_2O_3 films was evaluated using diverse mixtures of CF_4, O_2, and Ar gases, exhibiting superior resistance compared to sputter-deposited Y_2O_3 films. Additionally, we introduced the atomic layer annealing (ALA) process to increase grain size, achieving higher plasma etch reseistance. This study demonstrates that Y_2O_3 thin film coatings with ALD provides high plasma resistance in diverse etch conditions, preventing severe particle contamination during semiconductor manufacturing process.

AA-TuP-47 Atomic Layer Deposition of Copper Metal: Promising Cathode in Thin-Film Lithium-Ion Batteries, *Niloofar Soltani*, A. Bahrami, M. Hantusch, E. Dmitrieva, K. Nielsch, D. Mikhailova, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany

Since conversion and intercalation reactions during battery charging and discharging may cause substantial volume changes and irreversible structural transformations that severely affect cathode performance, copper metal has been shown to be a reliable substitute for conventional Li-ion hosting cathodes. However, similar to the shuttle effect in Li-S batteries, the main obstacle coupling Li and Cu is the deposition of reduced Cu^{2+} on the surface of Li during charging. In this study, the diffusion of Cu ions towards the Li foil was suppressed by employing a carbon-coated separator. Moreover, the high-rate capacity of 596 mAh g_{Cu}^{-1} at a current density of 837 mA g_{Cu}^{-1} was achieved by employing 100 nm thick Cu-film fabricated by atomic layer deposition (ALD), owing to its high surface area, which facilitated rapid redox reactions. With metallic Sb anode, a Cu-Sb full cell exhibits a reversible discharge capacity of 117 mAh g_{Cu}^{-1} (12.3 μAh cm^{-2}) at a relativity high current density of 837 mA g_{Cu}^{-1}. Constructing Cu thin films via ALD might open up new opportunities for replacing traditional Li ion-hosting cathodes in Li-ion microbatteries.

AA-TuP-49 Phosphite Doping of ALD SiO_2 Membranes Significantly Enhances Proton Conductivity for PEM Water Electrolysis, *M. Weimer, Sara Harris*, Forge Nano; *J. Jin, Z. Lin, K. Yim, L. Cohen, D. Esposito*, Columbia University; *A. Dameron*, Forge Nano

Water electrolysis powered by renewable sources can generate carbon-free, energy-dense hydrogen (H_2), to enable industrial decarbonization. Large-scale deployment of conventional alkaline and proton exchange membrane (PEM) electrolyzers is hindered by a higher levelized cost of H_2 by water electrolysis versus H_2 production by carbon-intensive steam methane reforming. To decrease this cost, overall cell efficiencies can be improved by reducing the ohmic overpotential required to drive proton (H^+) transport across the membrane, which is especially sensitive to membrane thickness.[1] Significant work has been done to reduce the thickness of Nafion membranes down to 50-200 um while keeping the safety-critical H_2 crossover below acceptable limits, but a fundamental limit to this path is apparent.[2] We have been exploring dense ALD SiO_2 as a proton conducting oxide membrane (POM) thinner than 1 um as a replacement. In this thickness regime, lower H^+ conductivities than Nafion are acceptable so long as the membrane material has lower H_2 permeabilities limiting H_2 crossover rates below maximum acceptable levels.[3] Baseline ALD SiO_2 POM had poor H^+ conductivity and superior H_2 permeability relative to Nafion-211 (24.5 um). To improve H^+ conductivity, novel P precursors were explored, as motivated by work on phosphorus-doped silica glass membranes.[4] Phosphate (PO_4^{-3}) species were successfully doped into the film across a range of temperatures, 100-250°C, using ABC-type ALD as measured by x-ray photoemission spectroscopy (XPS) and[4] substantial PO_4^{-3} incorporation required extended exposures below 250°C. Increasing PO_4^{-3} content was tracked by observing a red shift in the Si-O peak at 1100 cm^{-1} with Fourier transform infrared spectroscopy (FTIR), correlating XPS data. Figure 1 shows the inverse relationship of temperature with H^+ Conductivity for SiO_2 films with and without PO_4^{-3} doping. The best-performing membrane is PO_4^{-3} doped SiO_2 film deposited at 100°C with H^+ conductivity of **2.2×10^{-3} S/cm**, as measured by electrochemical impedance spectroscopy. This H^+ conductivity is almost an order of magnitude higher than previously reported ceramic membrane measured under the same conditions[5] and approaches the range of thin Nafion, 1.2×10^{-1} to 8.0×10^{-2} S/cm.[6] Importantly, H_2 permeabilities of the SiO_2 membranes remained ≈ 10^{-10} cm^2/s after PO_4^{-3} incorporation, while electronic leakage current remained low. Together, these results point towards the viability of PO_4^{-3}-doped SiO_2 ALD films as a promising material to realize sub-micron thick high H^+ conducting ceramic membranes for efficient and safe water electrolysis to enable a competitive green H_2 market.

AA-TuP-50 Deposition of Pt Nanodot on Carbon Powder Using Noble Pt Precursor and Stabilization of Nanodots, *T. Teramoto, C. Dussarrat,* K.K. Air Liquide Laboratories, Japan*; Nicolas Blasco,* Air Liquide Advanced Materials, France

Proton exchange membrane fuel cell (PEMFC) is a promising technology contributing to decarbonize industrial and societal activities by transforming chemical energy, typically hydrogen, into useful electric power in an efficient and clean way. Carbon-supported Pt catalyst is widely used for PEMFC applications due to its high electrochemical activities compared to other elements. However, the high cost of Pt catalyst is a significant hurdle to spread the commercialization of the large-scale utilization of PEMFC. Extending the lifetime of PEMFC is a conventional approach to improve the long term cost/performance of this technology. In this regard, several methods are attempted to improve durability of Pt catalyst on carbon support, for example, minimization of Pt nanodot agglomeration by precise size control of Pt nanodot, utilization of mesoporous carbon support, and applying metal oxide nanostructure formed by atomic layer deposition (ALD) around Pt nanodot.

This study proposes the low temperature formation (~150 $^{\circ}$C) of carbon supported Pt catalyst via the use of a novel precursor, so called Plato, with H_2 or O_2 as coreactant in a pulsed CVD process. The process temperature using the Plato precursor is much lower compared to the ALD process using Pt(MeCp)Me$_3$, typically around 250~300 $^{\circ}$C. The deposition of Pt nanodots was performed using Fluidized bed reactor (FBR) to achieve uniform and high dispersion of Pt nanodots on carbon supports. Transmission electron microscope (TEM) analysis indicates high dispersion of Pt nanodots on carbon support. Also, membrane electrode assembly (MEA) was prepared using the Pt/C catalyst samples made by Plato precursor and conventional Pt(MeCp)Me$_3$ precursor, and electrochemical performance using a test cell was evaluated. Also, area-selective ALD of metal oxide on a commercial Pt/C catalyst were attempted to enhance the stability of the catalyst.

AA-TuP-52 Hydrophilic Treatment of Porous PTFE Filter Membranes for Aggressive Chemical Environments, *Rubab Zahra, P. Kauranen,* LUT University, Finland*; M. Putkonen,* University of Helsinki, Finland

Polytetrafluoroethylene (PTFE) is a unique polymer with excellent thermal and chemical stability. However, PTFE is hydrophobic due to its low surface energy which restricts its use in applications where hydrophilicity is required. Achieving permanent hydrophilic modification of PTFE is a challenging task. Through atomic layer deposition (ALD) of inorganic oxides on PTFE substrates, it has been shown that the resulting material can survive extremely corrosive chemical environments while maintaining its hydrophilicity. In this study, we analyzed two samples of PTFE filter membranes with aspect ratios of 24 and 1000. PTFE surface was activated using ozone pretreatment and then ZrO_2 was deposited at three different ALD temperatures of 100, 150, and 200°C by using 300 cycles of tetrakis(ethylmethylamino)zirconium(IV) (TEMAZr) + oxygen source in Beneq TFS-200. Either H_2O or O_3 was used as an oxygen source. The pulse times were increased for PTFE filter membranes with an aspect ratio of 1000, to analyze its influence on the coating penetration depth. The effect of the selected oxidizer, film thickness, and deposition temperature was evaluated on the hydrophilicity and stability of membranes in an aggressive chemical environment. Using contact angle measurements, SEM/EDS cross-section analysis, water filling ratio inside the pores of samples, and thermal and chemical stability of coated membranes it was observed that ALD of ZrO_2 imparted permanent hydrophilicity and good coating penetration for PTFE sample with an aspect ratio of 24 whereas limitations in penetration depth for samples with a high aspect ratio of up to 1000 is discussed in detail. The findings of this study suggest that ALD can effectively enhance the hydrophilicity of PTFE without affecting its inherent chemical and thermal stability.

AA-TuP-54 Atomic Layer Deposition of Copper-Zinc Catalysts on Gas Diffusion Layers for the Electrochemical Reduction of CO$_2$, *Lovelle Manpatilan, S. Bianco, E. Tresso, S. Porro, J. Zeng,* Politecnico di Torino, Italy

Copper has been identified as an exceptional catalyst for the electrochemical reduction of CO_2 into value-added fuels and chemicals. By adding secondary metals such as Zinc, the product selectivity and performance of copper catalysts can be enhanced. This study presents Atomic Layer Deposition (ALD) as a novel technique for depositing Copper-Zinc electrocatalysts on Gas Diffusion Layers. ALD is a suitable deposition technique on microporous substrates due to its ability to provide uniform deposit thickness, precise stoichiometry control, and high substrate conformance.

Copper acetate, copper acetylacetonate, and diethyl zinc will be used as the metallic precursors, with water as the reactant. The ALD cycle ratio between the copper and zinc precursors will be tuned to control the Cu-Zn composition, and the optimum growth conditions will be identified. For comparison, separate Cu and Zn catalysts will be synthesized using ALD. The structural, morphological, compositional, and electrochemical properties of the Cu-Zn catalysts will be evaluated against the Cu and Zn catalysts to determine the effect of Zn addition to Cu. Finally, flow cells and membrane electrode assembly will be used to assess the selectivity, performance, and stability of the catalysts for CO_2 reduction.

This research is part of the European Union Horizon 2021 Marie Skłodowska-Curie Doctoral Networks (MSCA-DN) ECOMATES program for the "Electrochemical conversion of CO_2 into added value products via highly selective bimetallic MATerial and innovative process dESign". Furthermore, the research aims to contribute to the current understanding of ALD in electrochemical CO_2 reduction and facilitate the design of other copper-based bimetallic electrocatalysts in the future.

Note: Submission for the poster session, not the oral presentation

AA-TuP-56 New ALD Materials for DRAM/3D-DRAM Scaling, *Tejinder Singh,* Eugenus, Inc.

As the Semiconductor industry pushes the boundaries of power, performance, area and cost, Atomic Layer Deposition (ALD) solutions are required for the next generation of Logic, Memory & Packaging applications. In this presentation, we present new ALD materials for next-generation DRAM/3D-DRAM devices.

- **Application: DRAM Bitline Barrier Metal** - We present our ternary Ti-Si-N ALD film that has proven to have superior barrier properties for high temperature thin film providing an alternative to Physical vapor deposition (PVD). PVD based TiN film is a widely used diffusion barrier layer (Figure 1). However, deposition of ultra-thin TiN exhibits pronounced islanding which leads to rough film with polycrystalline grain structure. Furthermore, inhomogeneities due to grain boundaries offer diffusion pathways and lead to device degradation. We present our findings on the diffusion barrier properties of amorphous ternary alloy films composed of Ti, Si and N (TiSiN), an excellent alternative to TiN films. These films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial mini-batch reactor.

- **Application: DRAM Top & Bottom Capacitor Electrode:** We start with ALD TiN/TiSiN film and demonstrate it's step coverage with >98%. We then explore new materials for DRAM/3D-DRAM capacitor electrode such as VN/MoN deposited using ALD process in Eugenus 300mm single chamber multi-station reactor. ALD Molybdenum nitride (MoN) films were deposited via ALD using Mo solid precursor and NH3 at process temperature up to 550oC. The MoN film thicknesses were 4 to 12nm and characterized by various methodologies. Similarly, VN film was deposited using ALD process on non-pattern and pattern wafer with high aspect ratio (>90:1). Both MoN/VN show promising film properties such as higher Work Function and Lower Resistivity as compared to TiN and can be used for next-generation DRAM capacitor electrode.

- **Application: DRAM Capacitor High-k oxide:** One of the challenges for DRAM capacitor high-k oxide is to achieve >100% step coverage. However, current ALD processes can achieve 90% step coverage. We have developed a liquid precursor delivery ALD process module that can deposit several high-k ALD films with very high dielectric constant and step coverage > 100%. High-k films (ZrO/HfO) deposited have low leakage current, excellent step coverage, excellent uniformity, and accurate composition control.

In summary, this paper presents new materials (TiSiN, TiN, VN, MoN, ZrO, HfO, MoO) deposited in Eugenus ALD reactors to meet next-generation DRAM/3D-DRAM scaling challenges.

AA-TuP-57 Low Temperature Plasma-Enhanced Atomic Layer Deposited Boron Nitride Thin Films for Low-κ Dielectric Applications, *D. Le, S. De, T. Chu, J. Kim, D. Kim, M. Lee, M. Markevitch, Jiyoung Kim,* University of Texas at Dallas

To mitigate parasitic capacitance within the interconnect capping layer and/or inter-metal dielectric, the integration of low-*κ* dielectric materials is necessary for high-speed integrated circuit applications [1]. However, the inherent low density of such materials often compromises the material mechanical property during integration process [2]. Recently, boron nitride (BN) has been demonstrated as a potentialcandidate due to its high thermal conductivity and robust mechanical strength in comparison to

existing low-κ dielectric materials, such as boron carbon nitride (BCN) [3], silicon oxycarbonnitride (SiOCN) [4], etc. However, the conventional vapor-phase deposition process temperature requirement for BN (>400 C) is generally exceeding the BEOL compatible range.

In this study, we report a BEOL compatible highly conformal BN deposition process through plasma-enhanced atomic layer deposition (PEALD), in which tris(ethylmethylamino) borane (TEMA-B) and ammonia (NH_3) are employed as the metal and nitrogen sources. The deposition process is carried out within the range of 200–350°C. To validate the deposition of BN as well as material composition, X-ray photoelectron spectroscopy (XPS) is employed. Additional materials character techniques, including X-ray reflectivity (XRR), Raman spectroscopy, atomic force microscopy (AFM), etc., will be utilized to comprehensively evaluate the properties of the thin films. Furthermore, to determine the dielectric constant of BN, metal-insulator-metal (MIM) capacitors will be fabricated, with C-V and I-V measurements conducted for thorough characterization. The detailed experimental procedure and results will be presented.

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AA-TuP-61 Carrier Conduction Mechanisms in MIS Capacitors with Ultra-Thin Al₂O₃ at Cryogenic Temperatures, *Joel Molina-Reyes,* National Institute of Astrophysics, Optics and Electronics, Mexico

The study of the physical mechanisms associated with charge transport through thin Al2O3 films and the charge trapping phenomena are of great importance in the development of advanced Al2O3-based electron devices. These mechanisms have been studied at ambient temperature, as well as in temperature ranges above 300K. However, it is becoming highly relevant to consider cryogenic temperatures for these physical phenomena in order to develop devices for aerospace and cryoelectronic applications (like superconducting devices applied to sensing and quantum computing). In this work, a study comprising the electrical characterization and analysis of the electrical response of metal-insulator-semiconductor (MIS) Al/Al2O3/Si capacitors in a temperature range from ambient temperature down to 3.6 K is presented.

Ultra-thin Al2O3= 6, 2 nm were used as insulating layers by thermal ALD, thus ensuring high reproducibility in their physical and electrical characteristics. Current-voltage and electrical stress measurements were performed on the capacitors in the specified temperature range, and the experimental data obtained were analyzed using current transport equations to model the conduction mechanisms that allow charge transport through the Al2O3. Energetic parameters associated with trap levels within the Al2O3 bandgap corresponding to (1) trap-assisted tunneling and (2) direct-tunneling as main conduction mechanisms for 6 and 2 nm of

Al2O3 respectively, were obtained and their temperature dependences were associated with the presence of physical material defects. Additional phenomena that limit charge transport were also observed, such as (a) charge trapping in the bulk of Al2O3 upon the application of electrical stress at ambient temperature and (b) silicon freeze-out at cryogenic temperatures. For MIS devices, freeze-out represents the universal limit for carrier transport when silicon reaches 25 K. Our findings constitute an effort at understanding the physical phenomena that govern the electrical behavior of thin-film Al2O3-based capacitors, especially at cryogenic temperatures, given that these materials and devices are of great importance for applications in CMOS-based cryoelectronics and quantum technologies, among others.

AA-TuP-63 Alumina Coating of Diamond Filler Using Atomic Layer Deposition to Produce Thermal Interface Material, *Hiroya Ishida,* K. Shibuta, Sekisui Chemical Co., Ltd., Japan*; M. Groner, J. Gauspohl,* FORGE NANO, Inc.

Composite materials consisting of fillers and resins can provide performance or functionalities that single materials cannot, and so are widely used in industry. Examples include the thermal interface materials (TIMs) employed in various electronic devices for thermal management, for which there is a greatly increased demand. With the advent of 5G communications, large amounts of data must be transferred between devices and cloud-based services at high speeds. Associated semiconductor devices such as wireless communications antennas, CPUs and GPUs must

operate at high frequencies and so generate large amounts of heat, which can have a major impact on their performance and service life. TIMs are typically inserted between silicon dies and heatsinks or heat spreaders to release heat and so maximize performance. These materials are employed in smartphones, communications modules, automobiles, computer servers and industrial equipment. The thermal conductivity of TIMs directly affects the performance of semiconductors, and so the selection of an appropriate TIM is as important as the module and package design with regard to thermal management.

TIMs having high thermal conductivity allow flexibility in both the module design and assembly location. The use of appropriate materials is also a vital aspect of meeting market requirements and producing advanced TIMs with greater functionality and versatility. The thermal conductivity of a composite material is determined by both the filler and the resin, in addition to the filler proportion, as summarized by the Bruggeman model. Diamond has the highest thermal conductivity of all bulk materials, and so a high diamond filler content will increase the thermal conductivity of a composite. However, the limited compatibility of diamond with matrix resins limits the practical loading levels. Chemical modification of diamond surfaces to improve compatibility has been demonstrated but is still not well understood or sufficiently established. On this basis, the present study attempted to generate thin alumina coatings on diamond fillers using atomic layer deposition as a means of improving the compatibility of this filler with resins. The resulting alumina layers on diamond exhibited enhanced reactivity with silane compounds and increased the compatibility of diamond with a silicone resin without decreasing the thermal conductivity. Alumina-coated diamond specimens were also characterized in detail and the results are reported herein.

AA-TuP-65 Hf-Doped IGZO/IZO Heterojunction Thin-Film Transistors Fabricated by Atomic Layer Deposition for OLED Display, *T. Kim, Kang Min Lee,* Korea University, Republic of Korea

Metal oxide thin films, widely used as channel materials for thin-film transistors (TFTs), have advantages such as high transparency, low leakage current, high uniformity, and high on/off ratio, making them useful for driving display and flexible electronics. However, they still have a lower mobility than low-temperature polycrystalline silicon (LTPS) TFTs and require high temperatures annealing process (>300 °C). Notably, the process temperature needs to be reduced for operation at flexible substrates; however, this leads to a degradation in electrical properties.

To solve this problem, we developed a heterojunction oxide-based TFTs with planar and mesh-patterned channel layers, exhibiting enhanced flexibility and superior electrical characteristics. In addition, by utilizing Hf-doped IGZO/IZO heterojuction structures, we could improve the device bias stability with a low-temperature process. The incorporation of a mesh pattern expanded a quasi two-dimensional electron gas (q-2DEG) region, enhancing the TFT performance with flexibility. Moreover, when combined with OLEDs, the devices exhibited very operation in severe bending conditions, showcasing their usefulness for the future flexible display. More detailed results including transfer curve characteristics will be presented at the conference.

AA-TuP-66 Precise Tuning of Tamm Plasmon-Polaritons Resonances with sub-Nanometer Accuracy by Atomic Layer Deposition, *Mantas Drazdys,* E. Bužavaitė-Vertelienė, D. Astrauskytė, Z. Balevičius, Center for Physical Sciences and Technology, Lithuania

During the last decade, much attention has been given to photonic crystal (PC) structures covered with a thin metal layer on top of PC. A type of surface mode can be generated in PC-metal structures, the so-called Tamm plasmon-polaritons (TPP), appearing at the boundary between the PC and the metal layer. TPPs are optical states, which are similar to the electron states proposed by I. Tamm and can occur in the energy band gap at a crystal surface. These energy band gap regions are the stop band of the PCs due to the Bragg reflections in the periodic structure. The TPPs are non-propagating states which can be excited in both p- and s-polarizations. The optical dispersion properties of TPPs lead to simple optical configurations without additional couplers (prisms or gratings) which are necessary for excitations of well-known surface plasmon polaritons (SPPs). This opens new possibilities for various applications such as optical biosensors, bandgap filters, nanolasing, and others. For further technological progress in these applications, precise tuning of the optical properties of the TPP-based nanostructures as well as the plasmonic resonance position in the spectra is necessary, therefore, atomic layer deposition (ALD) is a very suitable technique with monolayer-by-monolayer growth of angstrom resolution. In this study, we demonstrate the potential capability to control

TPP by applying ALD as a highly precise technique for plasmonic applications. Spectroscopic ellipsometry and polarized reflection spectroscopy identified the TPP resonances in the photonic band gap (PBG) formed by periodically alternating silicon oxide and tantalum oxide layers. The TPP resonance dependence on Al_2O_3 layer thickness was evaluated, where 3 nm of Al_2O_3 layer thickness difference corresponded to ≈3 nm shift of TPP minima, demonstrating precise control capabilities when the ALD method is used.

AA-TuP-67 Rotating Drum ALD – an Alternative Approach for ALD Coating of Powders, *Mario Krug, M. Radehaus, M. Höhn,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany*; P. Heizmann,* University of Freiburg, Germany

Particle agitation is a crucial point for applying coatings on powder materials. Here, an alternative approach of a rotating drum within a tubular hot-wall reactor is presented. The rotating drum is a gas-flow-through-type drum offering a powder capacity of up to 100 cm^3. The powder agitation is realized by a special geometry in combination with the rotational speed of the drum. Different to a classical rotary kiln the rotating drum provides an easy-to-change and easy-to-clean option for batch processing under research and development conditions. A high freedom for experimental studies on a broad variety of powders is given by adjusting the powder particle agitation independently from the gas flow setting.

Moreover, this setup addresses important process capabilities, like tailor-made coating process designs, processing powders with broader particle size distributions and possibility of a gas phase pre- or post-treatment without vacuum break at temperatures of up to 1050 °C. Because of the modular design adaptations of the drum geometry, gas input and gas output openings as well as particle retention filters are possible without excessive effort using cost effective graphite as drum material which is passivated by a CVD-TiN coating. In case of the technological need of very thick coatings the transition from ALD to thermal CVD (standard or pulsed) can be realized using the same setup.

The experimental setup of the laboratory scale coating facility is described. Furthermore, the results of an example process of Al_2O_3- as well as AlTiO$_x$-coating on LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles (LNMO) are presented.

AA-TuP-69 Improving Ferroelectricity of Hafnia-Based Ferroelectrics by Adopting Anti-Ferroelectric Interfacial Layer, *Dae Haa Ryu, J. Lee, T. Choi,* Sejong University, Republic of Korea

Hafnia-based ferroelectrics (FEs) are one of the most promising candidates for next-generation non-volatile memory owing to their scalability and complementary metal-oxide-semiconductor (CMOS) compatibility. However, they have limitation in endurance properties which need to apply high operating voltage for switching ferroelectric polarization. On the other hand, hafnia-based anti-ferroelectrics (AFEs) have advantages for fatigue effect because their movement of defects are much smaller than ferroelectrics in phase transition. Furthermore, AFEs show high speed operation due to their rapid switching of polarization, unlike the gradual polarization reversal in ferroelectrics. In this study, AFE and FE Hf$_{(1-x)}$Zr$_x$O$_2$ (HZO) were consisted multi-layer heterostructure for utilizing their advantages (i.e., lower fatigue and non-volatile switching). In this structure, fatigue effect could be decreased without reducing its remnant polarization in few nano-meter thickness. By controlling the interface between AFE and FE materials, it is possible to reduce the leakage current, a critical issue in electronic devices of a few nanometers, caused by naturally formed suboxide.

Acknowledgements

AA-TuP-70 Atomic Layer Deposited p-type SnO Thin Film Transistors: Effect of Deposition Temperature on Device Performance and Stability, *Kham M. Niang, B. Bakhit,* University of Cambridge, UK*; J. Parish,* University of Bath, U.K.*; J. Driscoll,* University of Cambridge, UK*; A. Johnson,* University of Bath, UK*; A. Flewitt,* University of Cambridge, UK

Recently, p-type tin monoxide thin film transistors (SnO TFTs) produced by atomic layer deposition (ALD) has been gaining attention due to good reported device performance (field effect mobility, m_{FE} ~1 cm^{2}V^{-1}s^{-1}) and the relative ease in producing phase pure tin monoxide thin films when using a

Sn (II) containing precursor.[1] This is a promising step towards realizing complementary metal oxide semiconductor (CMOS) circuits using TFTs when combined with, n-type amorphous oxide (such as indium gallium zinc oxide) TFTs.[2,3]

Various novel Sn (II) precursors have been reported recently. The most commonly used of these is bis(1-dimethylamino-2-methyl-2-propoxy)tin,[4] and the corresponding TFTs show superior performance with m_{FE} ~ 1 cm^{2}V^{-1}s^{-1} and I_{ON}/I_{OFF} ~ 10^6 at maximum processing temperature of 250 °C.[1] We have also previously reported ALD SnO thin films using a new precursor called Sn (II) bis(*tert*-butoxide), with TFTs exhibiting m_{FE} ~ 0.6 - 2 cm^{2}V^{-1}s^{-1} and I_{ON}/I_{OFF} ~ 10^3- 10^4 after performing post annealing at temperatures between 250 - 350 °C.[5]

Here, we will report on further optimization of the ALD process conditions with this precursor including the deposition temperature and post-annealing temperature. We will show how these conditions affect the thin film morphology, grain size and the consequent TFT performances. We will also show how ALD technology allows us to easily and consistently produce SnO TFTs with either predominantly p-type conductivity or more pronounced ambipolarity. Finally, we will report the stability of the SnO TFTs under gate bias stress tests.

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AA-TuP-72 Oxide Based Neuron Devices Employing ALD Grown Dielectrics and Channel Layer, *Jung Wook Lim,* YUSEONG-GU GAJEONGDONG 218 ETRI, Republic of Korea*; J. Lee, C. Yu,* UST, Republic of Korea

Artificial neural networks has demonstrated remarkable performance in learning tasks and extensively explored in recent years [1-2]. However, due to substantial power consumption and the processing of massive data, a more efficient spiking neural network approach, mimicking the human brain, has emerged as an alternative, and active research is current underway. To address these challenges, research has been conducted on CMOS-based neuron devices [1]. However, due to the intricate structure, there is still a demand for the adoption of neuron devices using 1T (a single transistor) architecture non-silicon-based semiconductor materials. Our research group implemented synaptic devices based on oxide semiconductors, demonstrating excellent linear learning characteristics [3]. In this study, we aimed to realize the firing characteristics of neuron devices in a 1T structure concerning electrical stimulation by leveraging charge trap techniques employed in this research. The neuron device with a 1T structure features a bottom gate configuration, as illustrated in Figure 1. The semiconducting channel and dielectric layers were sequentially deposited using ALD, effectively trapping charges at the interface. Under regular and repetitive electrical stimuli with a consistent voltage magnitude and pulse duration, as positive charges become trapped, the transistor's transfer curve exhibits a rapid negative shift. Furthermore, with the continued accumulation of pulse stimuli, once surpassing a critical threshold, a sudden current flow occurs, leading to firing. When applying periodic stimuli to the gate electrode of the neuron device with a voltage of 11 V and varying pulse durations of 100, 300 and 500 µs, while maintaining a pulse interval of 300 ms, the firing patterns of drain current manifested as depicted in Figures 2 (a) to (c). The on/off ratio of the firing current was approximately 10^3, and as the pulse duration increased, there was a tendency for a decrease in the frequency of firing. As firing drain current needs to be converted to the voltage signal when transmitted to the subsequent synaptic devices in the neural network circuit, requiring a conversion of current signal to voltage signal by connecting a resistor, Figure 2 (d) shows the transformation of the current signal in Figure 2 (c) into a voltage signal. Although we successfully emulated the firing

characteristics of neurons with a 1T structure based on oxide semiconductors, the actual human brain exhibits more intricate firing patterns.

AA-TuP-73 MgF₂-Based Conformal Anti-Reflection Coatings on Highly Curved Lenses by Atomic Layer Deposition, *Yuma Sugai,* Shincron Co., Ltd., Japan; *H. Sugata, T. Sugawara,* Shincron Co. Ltd.,, Japan; *S. Muhammad, J. Hämäläinen, N. Lamminmäki, J. Kostamo,* Picosun Oy, an Applied Materials company, Finland

Anti-reflection (AR) coatings are crucial for a myriad of optical applications. The demand for conformal AR coatings over non-planar substrates, such as three-dimensional (3D) glass or curved lenses, is increasing. While physical vapor deposition (PVD) techniques—including electron beam evaporation and ion beam sputtering with planetary rotation—have been commonly employed for such AR coatings, these methods are struggling to maintain conformality over substrates with high aspect ratio, small dimensions or significant curvature. In response to these limitations, AR coating using Atomic Layer Deposition (ALD) emerges as a promising solution capable of achieving uniform coatings on such complex surfaces.

In this study, ALD was utilized to deposit multilayer AR films composed of MgF_2, SiO_2, Al_2O_3, and HfO_2. Notably, MgF_2 thin films are desirable for top layer due to their low refractive index (sub 1.4), wide spectral transparency from the ultraviolet to the infrared region, and considerable chemical stability. First, optimizing the thickness uniformity of the four distinct films using the Applied® Picosun® R-200 Advanced [1] was performed, then their individual optical properties were investigated. This information supported the design of a seven-layer AR film, and the AR layers onto substrates with highly curved lenses were subsequently deposited. Then, the optical performance of the coated lenses, focusing on reflectance was measured. Our measurements indicate that conformal AR coatings on lenses with pronounced curvature were successfully deposited. The research highlights the potential for achieving highly uniform AR coatings with precise optical control in areas such as medical optics, photonic integrated circuits, and meta-surface devices.

In conclusion, this study conclusively demonstrates the superiority of ALD-based AR coatings on complex geometric surfaces, offering an effective alternative to traditional PVD methods when confronted with their intrinsic constraints. With further optimization of the material stack and refinement of the deposition process, ALD presents a scalable and reliable avenue for fabricating novel AR coatings.

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AA-TuP-74 Enhanced Uniformity of Optical Films on Highly Curved Lenses using Atomic Layer Deposition for Small to Mid-Sized Batch Production, *Hironori Sugata, Y. Sugai, R. Sugawara, T. Sugawara,* Shincron Co., Ltd.,, Japan; *S. Muhammad, J. Hämäläinen, N. Lamminmäki, J. Kostamo,* Picosun Oy, an Applied Materials company, Finland

In the field of optics, the generation of anti-reflective (AR) coatings on high-curvature convex lenses, crucial for various applications, has been predominantly realized through Physical Vapor Deposition (PVD) methods like evaporation and sputtering. While conventional PVD techniques with planetary rotation can achieve a non-uniformity (NU) ≤ 5% on lenses over 30 mm in diameter, maintaining thickness uniformity remains a challenge. Notably, Atomic Layer Deposition (ALD) equipment manufacturers typically advertise coating NUs of 1% to 3% over flat substrates, with claims of conformal coating over 3D structures [1]. However, uniformity can vary with material and process conditions, and there is a lack of detailed literature on uniformity achievements in ALD mass production. Our study demonstrates marked improvements in film thickness uniformity through ALD for small to mid-sized batch processing.

In this study, a R-200™ Advanced ALD system, manufactured by Picosun Oy (Espoo, Finland,) was utilized to conduct a small-scale batch test run. A custom fixture was designed, allowing simultaneous deposition of a single-layer 300nm thickness SiO2 on 36 convex lenses. Thickness uniformity was evaluated using the USPM-RU-W NIR Microspectrophotometer from Olympus Corporation (Tokyo, Japan), capable of precise reflectivity measurement at the micro-spot level. The lenses were mounted on a tilt stage to ensure perpendicular light incidence relative to the lens surface by fine-tuning x, y, and z positioning.

Our results indicated intra-lens NU of ≤ 1.2% within the optimally coated regions of the batch. Across the entire batch, NU was maintained at ≤ 5.0%. The findings underscore the capability of the Picosun® downflow thermal ALD system to achieve uniform coatings suitable for small to mid-sized

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AA-TuP-75 Enhancing the Stability of p-Type Tin Monoxide Thin Film Transistor Through 2D Structure Optimization via Discrete Feeding Method, *Haklim Koo, H. Kim, S. Choi, W. Lee, S. Kim, J. Park,* Hanyang University, Korea

Oxide semiconductors have a wide range of applications in electronics, including displays, semiconductors, and sensors, due to their exceptional electrical properties. These properties include high mobility, low off-current, and excellent uniformity. However, achieving high electrical performance in p-type oxide semiconductors is challenging due to the delocalized hole conduction path and difficulty in carrier formation mechanisms. Tin monoxide (SnO) is a promising p-type material among several candidates. This is due to its low formation energy of tin vacancies (V_{Sn}) and high hole mobility resulting from the delocalization of the hole conduction path. However, the SnO structure has low thermal stability, and it can easily undergo a phase transition to n-type tin dioxide (SnO_2). Therefore, it is important to study fabrication methods to obtain stable SnO. Several studies have reported the formation of SnO through sputtering. However, fabricating stable SnO thin films is challenging due to the narrow process window and occurrence of phase mixing. Recently, ALD has gained attention in research due to its advantages. ALD is preferred over sputtering methods due to its highly conformal growth in high aspect ratio structures and low damaging effects, making it suitable for 3D stacked devices.

In this study, we suggested that the 2d structure of c-axis aligned tetragonal SnO could be improved by controlling the precursor feeding process by evaluating water contact angle and grazing-incidence wide-angle X-ray scattering (GIWAXS) (Figure 1). Through controlling the precursor feeding method, which divides the dosing step into several stages, surface coverage was improved, and c-axis crystallinity was enhanced, which has fewer structural defects by optimizing horizontal crystal growth. As a result, it was confirmed that excellent reliability characteristics were obtained, and the thermal reliability of SnO-TFT, which had never been previously reported, was also confirmed to have outstanding characteristics. SnO-TFT we manufactured has an excellent reliability of +0.33 V and -0.25 V in P(N)BS (±2 MV/cm, 3,600s, RT), +0.47 V and -0.11 V in P(N)BTS (±2 MV/cm, 10,000s, 60℃). In addition, we have successfully fabricated a flexible SnO-TFT with a Vth change of only 0.06V even after 10,000 cycles of bending test with a curvature radius of 0.5cm (Figure 2). Through this process optimization research, we will be able to secure the stability of the SnO thin film and realize stable operation of the p-type oxide semiconductor, thereby promoting the application of oxide semiconductors to various industries such as displays.

AA-TuP-76 Resistive Switching in Hafnium-Titanium-Oxide Thin Films Grown by Atomic Layer Deposition, *Toomas Daniel Viskus, J. Merisalu, A. Kasikov, L. Aarik, K. Kukli,* University of Tartu, Estonia

Resistive switching has been previously studied in both titanium oxide [1] and hafnium oxide[2] metal-insulator-metal (MIM) structures. Devices utilizing TiO_2/HfO_2 bilayers have also been studied [3].

We investigated resistive switching properties of devices where TiO_2:HfO_2 mixed oxide dielectric layers were grown by ALD on RuO_2 bottom electrode with Pt top electrodes. The electrodes were deposited using magnetron sputtering. ALD was carried out at 350 °C. The precursors used were $HfCl_4$, $TiCl_4$, H_2O. Multiple samples with a varying ratio of TiO_2 to HfO_2 deposition cycles were prepared. For each ratio, both an as-deposited sample and a sample annealed for 30 minutes at 400 °C were evaluated.

GIXRD measurements showed that, as the HfO_2:TiO_2 ALD cycle ratio grew, one could at first observe the transition from the TiO_2 rutile phase to the $HfTiO_4$ orthorhombic ternary phase, followed by further transition the monoclinic HfO_2.

Electrical measurements were carried out using a Cascade Microtech EPS-150 probe station and a Keithley 2636A source-meter. All studied samples showed resistive switching properties. As-deposited devices with the $HfTiO_4$ orthorhombic phase and a HfO_2:TiO_2 ratio of 1:3 demonstrated ratio between the low resistance state (LRS) and high resistance state (HRS) about 10, with an endurance measurable up to thousands of cycles. Retention measurements were carried out at variable temperatures, up to 140 °C, for 6 hours and showed good stability for both LRS and HRS.

Preliminary device-to-device repeatability tests were also carried out and showed that annealed devices demonstrated better repeatability when compared with non-annealed devices.

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AA-TuP-78 Comparative Study of ZrAl$_x$O$_y$ - based MIM Decoupling Capacitors with high-κ Dielectric Grown by 3 Generations of Metalorganic ALD Zr-precursors, *Konstantinos Efstathios Falidas, K. Kühnel, A. Viegas, M. Czernohorsky,* Fraunhofer Institute for Photonic Microsystems (IPMS), Germany

Decoupling capacitors provide stable capacitance over voltage, allowing good voltage regulation and noise immunity. Typically placed in BEoL, these MIM capacitors rely on high-κ dielectrics deposited through ALD. Zirconium oxide, a well-established oxide since DRAM times, is commonly doped with Al in alternating laminates. This doping strategy aims to control crystallization, minimize leakage, and enhance capacitor's operational lifespan. The selection of appropriate metal precursors becomes pivotal in achieving optimal electrical properties that align with strict industrial standards.

This study presents a comparative analysis of 3 "generations" of metalorganic Zr-precursors employed in planar MIM capacitors. The explored Zr-precursors include 1st generation TEMAZr, 2nd generation Air Liquide ZyALD™ and the recently synthesized 3rd generation Air Liquide Kaze. Ozone serves as reactant agent and Ar as purge gas. Given the novelty of Kaze's various ALD parameters, such as deposition temperature (T$_D$), purge time, oxidant time are systematically adjusted to achieve stable performance and properties comparable to existing precursors in BEoL (T$_D$≤400°C). Additionally, the step coverage of the last 2 generations is compared to facilitate Kaze's application in deep 3D capacitors. Kaze exhibits coverage slightly better than its predecessor.

For ZrAl$_x$O$_y$ stacks, Al is introduced using Trimethylaluminum. Kaze's uniformity and carbon impurities saturate at T$_D$≤400°C. Therefore, 2 T$_D$ (350°C, 400°C) were further examined. Beyond chemical and structural analysis, MIM stacks are fabricated on 300 mm wafers incorporating TiN electrodes on both sides. Their electrical characteristics are scrutinized, considering parameters such as capacitance density and field linearity (α) across varying temperatures and frequencies. Across all 3 generations, C$_0$ exhibits stability over frequency (1-100 kHz). Higher T$_D$ for Kaze$_{400°C}$ demonstrates a 62.5% lower α compared to Kaze$_{350°C}$. In comparison to TEMAZr, Kaze showcases a notable 93.7% improvement in α. Given the paramount importance of α for decoupling purposes, the decrease in C$_0$ is considered negligible. Moreover, studies are conducted on leakage, breakdown, and reliability. Both J-E curves and E$_{BD}$ reveal for all 3 generations consistent and analogous behavior over a broad temperature window (25-125°C). The extrapolated lifetime of Kaze at T$_D$=400°C and under maximum temperature stress, exceeds the performance goal of 10 years under operating field conditions, indicating Kaze as a competitive precursor for Zr-based decoupling capacitors.

AA-TuP-79 ALD Capping Layers for Copper Redistribution Lines, *Ritwik Bhatia,* Veeco; *E. Chery,* imec, Belgium; *G. Sundaram,* Veeco; *N. Pinho, E. Beyne,* imec, Belgium

Chiplet based architectures have enabled integration of diverse chips (memory, logic, AI accelerators etc) into a high-performance package. Copper redistribution lines (RDL) enable connections between chiplets by moving power and signal lines to locations better suited for inter-chip bonding. One of the most promising approaches relies on the patterning of copper lines embedded in a polymer matrix [1]. Unfortunately, polymers are generally not good barriers against oxygen and moisture diffusion [2]. This makes the copper lines prone to oxidation (Figure-1, 3a) which is especially problematic as the width of the copper line becomes smaller [2].

In this study, ALD thin films, deposited at 100 °C, are evaluated as an oxidation barrier via high temperature storage (HTS) - 150°C for 1000 hours. Al2O3 is shown to be as good a barrier at 15nm as it is at 50nm (Figure-2). Thin capping layers are of primary importance, as they allow connections to the above metal layer through a simple sputter etch process to reopen the ALD film and land a via. ALD HfO2 is also found to be a good barrier, while TiO2 is not. Long term reliability testing (HTS for more than 2000 hours, corrosion testing (85-85 humidity + HTS) and temperature cycling) of daisy chained copper lines with ALD Al2O3-TiO2 as a barrier layer show no change in the resistance value (Figure-3b) confirming the ability of the ALD layer to fully block the oxidation of the copper lines. This indicates a very high quality of barrier performance.

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AA-TuP-80 Incipient Ferroelectric Properties in as-Deposited Hafnium Zirconium Oxide for BEoL Applications, *Alison Erlene Viegas,* Fraunhofer Institute for Photonic Microsystems (IPMS) - CNT, Germany; *K. Kuehnel,* Fraunhofer Institute for Photonic Microsystems (IPMS)- CNT, Germany; *S. Yang, K. Falidas,* Fraunhofer Institute for Photonic Microsystems (IPMS) - CNT, Germany; *M. Czernohorsky,* Fraunhofer Institute for Photonic Microsystems (IPMS)- CNT, Germany

The discovery of ferroelectric properties in doped hafnium oxide in 2011, has driven forward the research in the development of ferroelectric hafnium oxide devices. The ferroelectric phase can be stabilized by dopants, mechanical strain and annealing conditions. For application such as ferroelectric memories, a key issue is the wake-up effect, which means that the device has to be pre-stressed before the actual operation. Doping hafnium oxide with zirconium, makes it possible to fabricate devices in the Back-End-of-Line (BEoL), as the crystallization and annealing conditions are well within the BEoL restrictions.

In this paper, we report the development of the ferroelectric properties with as deposited hafnium zirconium oxide (HZO) using a new generation of metalorganic precursors, Air Liquide's Kahe and Kaze for hafnium and zirconium respectively, designed to be operated at higher temperatures. With higher deposition temperatures, and a slow growth rate, the deposited HZO samples are crystallized in the metastable ferroelectric phase during deposition. Different ratios of hafnium to zirconium are deposited under varying deposition temperatures, to determine the optimum concentration for ferroelectricity. Higher deposition temperatures could also provide the possibility to deposit in high aspect ratio structures with good step coverage. The films are characterized by ellipsometry, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and X-ray photon spectroscopy (XPS) for the material properties. The XRD patterns show that the as deposited samples, for different ratios of Hf:Zr (deposited at 350°C), are already crystalline in the ferroelectric orthorhombic phase, without any signatures of monoclinic phase. The electrical properties were tested by depositing the material between two sandwiched titanium nitride electrodes in the form of a metal-insulator-metal capacitor. Initial testing reveals a wake-up free HZO samples with good memory window of 29.8 μC/cm^2 at 10^5 cycles.

AA-TuP-82 Exploring Brookite Phase Formation in Vanadium Oxides by Atomic Layer Deposition for Uncooled Infrared Sensor Applications, *Hyeonho Seol, S. Lee,* Kyung Hee university, Republic of Korea; *W. Jeon,* Kyung Hee University, Republic of Korea

Vanadium oxide has been extensively studied as a material for the microbolometer of uncooled infrared sensors. Previous research has highlighted its high reactivity, as evidenced by the high temperature coefficient of resistance (TCR) value at room temperature [1]. Vanadium dioxide (VO$_2$) exists in various crystalline phases, including monoclinic, brookite, and rutile phases [2]. The monoclinic phase, which is the most stable phase of vanadium dioxide, undergoes a semiconductor-to-metal transition known as the Mott transition at 67°C, rendering it unsuitable for use as an infrared detection layer for microbolometers over a wide temperature range [2]. In contrast, the brookite phase does not exhibit the Mott transition over a wide range around room temperature, making it suitable for use in infrared detection sensors.

In this study, we developed an atomic layer deposition (ALD) process for VO_2 with a brookite crystal structure, which is a metastable phase among its polymorphs. We investigated the characteristics of vanadium oxide thin films under various process conditions, including deposition temperature, using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF). TCR evaluation was conducted through resistance measurements at temperatures ranging from 30°C to 100°C. The brookite phase was predominantly obtained at higher deposition temperatures, and it was revealed that the formation of the brookite phase was attributed to the presence of excess oxygen in the vanadium oxide thin film [3].

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AA-TuP-83 In-Situ ALD Fabrication of Heterogeneous Gate Insulators for Improved Reliability in High-Mobility IGZO Transistors, *T. Hwang, Y. Kim, H. Oh, Jin-Seong Park, Hanyang University, Korea*

Since their 2004 introduction by the Hosono group, oxide semiconductors (OS) represented by IGZO have revolutionized thin film transistor (TFT) technology, favored in the display industry for their transparency, uniformity, cost-effectiveness, low processing temperatures, high mobility, and extremely low off current. Atomic layer deposition (ALD) plays a key role in improving OS device characteristics by offering precise control over film thickness and composition of complex 3D structures, and the deposition of high-quality films. Yet, the high mobility of OS TFTs presents reliability challenges because OS is sensitive to impurities and defects like hydrogen and CO-related impurities. To fabricate a high-mobility and high-reliability OS device, not only the design of the active layer but also the process design surrounding the active layer must be followed. Inspired by the idea that internal defects in gate insulators and donor-induced species have opposite effects on threshold voltage shifts, we propose a novel approach to improve device reliability by in situ ALD stacking two gate insulators, each corresponding to one mechanism, with the reliability compensation that cancels out the two mechanisms. This strategy significantly enhances device reliability, mitigating the adverse effects of impurities and defects, and represents a significant breakthrough in semiconductor technology.

In this study, we enhance the reliability of high-mobility (>50 cm²/Vs) ALD-IGZO top-gate transistors by employing a meticulously designed heterogeneous gate insulator, using an in-situ ALD process. We developed a heterogeneous (SiO_2/Al_2O_3) gate insulator, exploiting the distinct reliability mechanisms of opposing threshold voltage shifts in Al_2O_3 and SiO_2 to neutralize the net reliability change within the transistor. Aimed at minimizing the impact of opposing charges, this method has been applied to high-mobility ALD-IGZO transistors, achieving significant improvements in positive-bias-temperature-stability (ΔV_{th} = -0.02 V) and constant-current-stability (ΔI_D = 100.49 %). In conclusion, our investigation into reliability compensation, characterized by electron trapping in the gate insulator and compensation of shallow donor generation in the active layer with hydrogen defect passivation, provides profound insights into overcoming the reliability challenges typically associated with high-mobility ALD-OS TG transistors. This innovative, heterogeneous gate insulator design, rooted in an in-situ ALD process, offers a significant advancement in addressing the reliability issues of high-mobility ALD-OS TG transistors.

AA-TuP-84 Broadband Anti-Reflective Coatings with Graded Refractive Index on Plastic Optics, *Philip Klement, M. Zscherp, H. Spielvogel, A. Henss, S. Chatterjee, Justus Liebig University Giessen, Germany*

Plastic optics made from acrylic glass or polycarbonate are widely utilized in various applications such as eyeglasses, cell phone cameras, windows, and displays due to their light weight, cost-effectiveness, and ease of manufacturing. However, achieving broadband, omni-directional, and durable anti-reflective (AR) coatings for these plastics poses challenges with conventional deposition methods. These challenges include limitations in process temperatures, damaging surface modifications induced by process plasma, and the absence of robust chemical bonding between the coating and the plastic.

In this study, we introduce nanoporous alumina coatings with a graded refractive index on plastic optics to address these challenges. By employing Atomic Layer Deposition (ALD) of alumina on poly (methyl methacrylate) or polycarbonate followed by immersion in hot water, we fabricate grass-like alumina structures. This approach yields outstanding AR-performance, achieving a remarkable reduction of the residual reflectance to 0.3% in the visible range (400–900 nm) for a single-sided coating. Angular spectral reflectance measurements (0–70°) confirm the omni-directional nature of the AR coating with minimal residual reflectance across all angles of incidence.

Furthermore, the infiltration of trimethylaluminium and water into the polymer substrate during the ALD process forms rigid chemical bonds between the polymer and alumina, resulting in durable coatings. We investigate the depth of Al infiltration into the polymer as a function of process time and find an enhancement in AR performance attributed to the formation of an additional graded refractive index at the coating-substrate interface.

The exceptional AR performance, ease of processing, strong adhesion to various optical plastics, and compatibility with commercial deposition systems make this AR technology highly promising for practical applications.

AA-TuP-86 Effect of Sn-doping on Atomic-Layer-Deposited Ultrathin In-Sn-O Thin-Film Transistors, *Binbin Luo, S. Ding, Fudan University, China*

Indium oxide (In_2O_3) thin film transistors (TFTs) have attracted much attention for back-end-of-line (BEOL) compatible logic and memory applications towards monolithic 3D integration. Despite its excellent device performance, some challenges still exist for In_2O_3 TFTs such as high off-current (I_{OFF}), easy crystallization (cubic structure) and instability. Doping with metal cations (e.g., Ga, Zn, Al, W, Ti, Si) is an effective method to resolve these issues in the sputtering-derived In_2O_3-based TFTs. Compared to other elements, Sn with tetragonal structure (SnO_2), similar radius, and high binding energy with oxygen (531.8 kJ/mol) is a promising candidate, which is expected to not only inhibit crystallization but also enhance stability and mobility. In addition, InSnO (ITO) exhibits a lower permittivity of around 4 compared with IGZO (~16), which effectively reduces short-channel-effect (SCE). The atomic layer deposition (ALD) technique enables precise control of both the thickness and wafer-scale uniformity of the In_2O_3-based thin films. Besides, ALD can conformally deposit ultrathin films in nanoscale on three-dimensional (3D) structures such as sidewalls and deep trenches, which is a key technology for downscaling devices and monolithic 3D integration. This work focuses on the fabrication of high-performance ultrathin amorphous ITO TFTs using plasma-enhanced ALD (PEALD). Firstly, we obtained the temperature window and growth rate of PEALD In_2O_3 and SnO_2 films, where $In(CH_3)_3$ (TMIn) and $Sn(N(CH_3)_2)_4$ (TDMASn) were used as metal precursors for In and Sn. Then, we systematically investigated the effects of Sn-doping on the crystal structure of ITO films and the electrical performance of ultrathin (~3 nm) ITO TFTs. The compositions of ITO thin films were tuned by changing the cycle ratio of In_2O_3 to SnO_2 (In:Sn). It is found that Sn is an effective dopant to inhibit crystallization of In_2O_3, decrease V_O and increase mobility, but excessive Sn doping degrades the electrical performance of TFT. Among the various compositions, the TFT with In:Sn=7:1 channel demonstrated optimal electrical characteristics(μ_{FE} =54.8 cm²/Vs, V_{th} = -0.67 V, SS = 91 mV/dec, I_{ON}/I_{OFF} = ~10⁹). Our work provides a promising candidate for BEOL compatible transistors in monolithic 3D integration.

AA-TuP-87 Processing and Performance of Piezoelectric Lead Hafnate-Titanate Thin Films Grown by Atomic Layer Deposition for 3D MEMS Actuators, *Nicholas Strnad, DEVCOM Army Research laboratory; R. Knight, R. Rudy, DEVCOM Army Research Laboratory; A. Parrish, D. Wang, A. Shkel, University of California, Irvine; J. Pulskamp, DEVCOM Army Research Laboratory*

Lead hafnate-titanate ($PbHf_xTi_{1-x}O_3$, PHT) is a ferroelectric and piezoelectric ceramic that is a structural isomorph of lead zirconate-titanate (PZT), a well-studied and commercially relevant multifunctional material, and exhibits very similar electromechanical properties. Thin film PZT has been implemented commercially in MEMS printheads and in ferroelectric random-access memory (FRAM). PZT is also utilized for MEMS actuators, MEMS sensors, and energy harvesters. 3D implementation of either ALD PZT or PHT can offer functional thin films with 200x+ material volume fill per unit area that scales with the device surface-area (e.g., trench or nanopore depth and pitch), offering larger piezoelectric or ferroelectric energy densities in a small footprint. Alternatively, 3D implementation of ALD PZT or PHT can be used to fabricate actuators on sidewalls or curved surfaces where they may deliver forces more effectively or enable new axes of motion for MEMS. Despite the large technological potential of 3D piezoelectric films, there are few reports of ALD processes for piezoelectric thin films and scant reports on applications or prototypes. Here, we present results of a novel ALD process for PHT using oxygen as a co-precursor on

platinized silicon wafers and implement the PHT as a 3D actuator on curved glass-blown micro-scale hemispherical resonators. The resonators are a fundamental component of micro-scale hemispherical resonating gyroscopes (µHRGs) which are being explored as a high performance and low-cost alternative to traditional navigation-grade inertial sensors. (1) We will present precursor dose saturation curves for the PHT process, PHT thin film material characterization, and piezoelectric characterization of the 3D actuator using laser doppler vibrometry (LDV) measurements of the resonator displacement. Equally important, the PHT also displayed excellent ferroelectric properties, and exhibited a 2Pr of 68 µC/cm² and a max polarization of +/- 78 µC/cm² at +/- 8V, respectively.

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AA-TuP-88 Stacked ALD Deposited Metal Oxide Films as Reliable Sensing Films for Organic Semiconductor-Based LAPS, *Chia-Ming Yang*, Y. Yang, Chang Gung University, Taiwan; *B. Jiang, C. Chen,* Ming-Chi University of Technology, Taiwan

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Light-addressable potentiometric sensor (LAPS) had been proven for chemical and bio sensing with ability of 2D imaging and easy fabrication. Recently, organic semiconductor had been proposed for the semiconductor layer of LAPS with advantages of high absorption, low-temperature process, capability of flexible substrates. However, restrictions are the stability and lifetime due to the electrolyte environment degraded the insulator/sensing membrane of LAPS. This research focuses on fabricating stacked aluminum oxide (Al_2O_3) and hafnium oxide (HfO_2) using an atomic layer deposition (ALD) system for sensing membrane to improve the stability and lifetime of organic semiconductor-based of LAPS.

A zinc oxide (ZnO) layer was applied to serve as the electron transport layer by spin coating on indium tin oxide (ITO)/glass. An organic material layer with composition of PTB7-Th and $PC_{71}BM$ were mixed then deposited on the ZnO using a spin coater. Different metal oxide including Al_2O_3 and HfO_2 with thickness of 6 nm for each layer to total thickness to be 24 nm were deposited by ALD to function as sensing films. The standard photocurrent versus bias voltage (PC-V) curves triggered by red laser (e.g., 658 nm wavelength) were collected in various sensing requirements including sensitivity, hysteresis and drift measurements for LAPS. In pH range from 2 to 10, the linearity and sensitivity of stacked ALD LAPS device is 99.7% and 50.7 mV/pH, respectively. The hysteresis width was -13.2 mV. Stacked ALD structure makes organic semiconductor-based LAPS can survive for whole drift measurement for 12 h and owns a drift coefficient of 3.26 mV/h, which approaches to basic requirement of inorganic semiconductor-based LAPS.

The employment of a multilayered configuration does offer a significant electrolyte-proof improvement, contributing to the device's overall durability and extending the possibility of 2D chemical imaging of organic semiconductor-based LAPS. This technique could ensure that organic materials to be utilized and maintained in LAPS structure and similar field-effect sensing devices for extended durations, thereby increasing their longevity and reliability.

AA-TuP-89 Effects of TiO₂ Incorporation via Atomic Layer Deposition on Yttria-Stabilized Zirconia Electrolyte for Energy Storage, *Jorge Luis Vazquez Arce,* El Centro de Investigación Científica y de Educación Superior de Ensenada, Baja California, Mexico; *C. Bohórquez Martinez,* UNAM, Mexico; *A. Bahrami,* Leibniz Institute for Solid State and Materials Research, Germany; *E. Blanco,* Universidad de cadiz, Spain; *M. Dominguez,* Universidad de Cadiz, Spain; *K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany; *G. Soto Herrera, H. Tiznado,* UNAM, Mexico

Electrolyte material optimization is crucial for electrochemical energy storage devices. The specific composition and structure have an impact on conductivity and stability, both of which are essential for efficient device performance. The effects of controlled incorporation of TiO_2 into Yttria-Stabilized Zirconia (YSZ) electrolyte using the atomic layer deposition (ALD) technique are investigated in this study. The surface chemical composition analysis reveals variations in the Ti oxidation state and a decrease in the O/(Zr+Y+Ti) ratio as TiO_2 concentration increases. The formation of acceptor states near the valence band is proposed to reduce the bandgap with the Fermi Level. The structural properties indicate that as TiO_2 concentration increases, surface homogeneity and crystallite size increase. The contact angle with water indicates a hydrophobic behavior influenced by surface morphology and potential oxygen vacancies. Finally, electrical properties, measured in Ru/TiO_2-doped YSZ/Au capacitors operated at temperatures between 100 and 170 °C, showed that the TiO_2 incorporation improved the ionic conductivity, decreased the activation energy for conductivity, and improved the capacitance of the cells. This study highlights the importance of the ALD technique in solid-state electrolyte engineering for specific applications such as energy storage devices.

AA-TuP-90 Dynamic Color Shifting of Green Organic Light-Emitting Diodes Utilizing Distributed Bragg Reflector Mirror Fabricated via Atomic Layer Deposition, *Junbeom Song,* J. Bi, Korea University, Republic of Korea; *Y. Park,* Sun Moon University, Republic of Korea; *B. Ju,* Korea University, Republic of Korea

Organic Light-Emitting Diodes (OLEDs) have garnered considerable interest owing to their benefits such as easy manufacturing process, wide viewing angle, low unit price and energy consumption, and thin and flexible form factor compared to liquid crystal displays (LCDs). However, a notable drawback of blue OLEDs is their shorter lifetime compared to green or red OLEDs, primarily due to their higher energy consumption. To address this issue, researchers are exploring various methods involving both materials and structural modifications.

Among these approaches, there is ongoing research aimed at leveraging the longer lifespan and higher stability of green OLEDs to generate other colors. In this study, we focus on modeling and fabricating OLEDs using a distributed Bragg reflector (DBR) model, utilizing atomic layer deposition (ALD). DBR involves depositing alternating layers of high and low refractive index thin films, exploiting total internal reflection (TIR) at each interface to achieve high reflectivity. By using DBRs, composed of Al_2O_3 and TiO_2, which exhibit high reflectivity due to their difference in refractive index, we could adjust the number of pairs to model specific spectral light.

Through comprehensive simulation, we verified that Alq_3, a green, fluorescent material with a peak emission wavelength at 564 nm (Fig 1a), could effectively shift green to a blue component with a peak emission wavelength at 478 nm by employing a 2-pair DBRs (Fig 1b). Additionally, in Figure 2, we verified that reducing the full width at half maximum (FWHM) from 182 nm to 42 nm enables the extraction of a highly pure blue color. Based on these simulation results, we are conducting experimental design and characterization to ensure the fabrication of devices matching the simulated properties. The electroluminescence (EL) characteristics of the device without a DBR show a peak wavelength at 554 nm (Fig. 4), which is similar to the simulation results. This indicates that including a DBR in the device is expected to result in a shift towards the blue wavelength region. This research contributes to advancing the understanding and utilization of novel techniques in OLED technology, paving the way for enhanced performance and longevity in display applications.

AA-TuP-91 Ultrathin TiN/TiO₂/Ti Solar Absorbers Enabled by Atomic Layer Deposition, *Luca Mascaretti,* Czech Technical University in Prague, Czech Republic; *A. Naldoni,* University of Turin, Italy; *L. Kalvoda, I. Richter,* Czech Technical University in Prague, Czech Republic

Solar-thermal conversion is an attractive strategy to collect sunlight and transform it into heat that is directly utilized or further transformed into electricity.[1] Depending on the specific route, solar absorber materials must be carefully designed to achieve the highest solar absorptance and to withstand severe thermal cycling. For example, metal-insulator-metal (MIM) metasurfaces based on titanium nitride (TiN) demonstrated nearly unitary absorption and stability under annealing and focused light irradiation.[2] In this contribution, we discuss a simple continuous and scalable MIM absorber based on TiN/TiO_2/Ti. We first discuss the optimization of optical absorption by numerically computing optical spectra for different values of the TiN and TiO_2 thickness in the ranges 0–35 nm and 0–75 nm, respectively. As a result, the optimized structure TiN (10 nm)/TiO_2 (50 nm)/Ti exhibits ~ 60% optical absorption in the 250–2000 nm range, outperforming a counterpart based on Au. Such optimized structure is then experimentally realized by the atomic layer deposition (ALD) technique by using the $TiCl_4$ precursor combined with H_2O (thermal process for TiO_2) and N_2 plasma (for TiN). We further discuss additional effects that can additionally increase the optical absorption up to ~75%, such as surface

oxidation of the ultrathin TiN layer, which affects its permittivity.[3] Therefore, the combination of such Ti-based materials allows the realization of a solar absorber without further need of surface patterning, highlighting the potential of ALD for solar energy applications.

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AA-TuP-92 Simultaneous Enhancement in Performance and Stability of LSCF Air Electrode of Reversible Solid Oxide Cell by Atomic Layer Deposited CeO₂ Coating, *Sung Eun Jo, K. Ju, H. Kim, W. Park, J. An,* Pohang University of Science and Technology (POSTECH), Republic of Korea

Atomic layer deposition(ALD) offers the ability to conformally coat intricate structures at atomic level. Widely adopted in the semiconductor industry, ALD stands out as a beneficial technique for enhancing the performance and durability of electrochemical devices(battery, fuel cells) Surface engineering via protective, catalytic nano-layer by ALD, durability and performance of electrochemical devices increases.

Reversible solid oxide cells(rSOSs) are energy conversion devices between chemical energy(hydrogen) and electrical energy, which operate both in fuel cell mode(solid oxide fuel cell : SOFC) and in electrolysis mode(solid oxide electrolysis cell : SOEC). rSOCs show high thermodynamic efficiency, fuel flexibility, and scalability; however, their high operation temperature, typically exceeding 800°c, causes rapid degradation at the electrode surface which is usually composed of perovskite materials. Particularly in rSOCs, the thermal degradation of air electrode by A-site dopant material(Sr) segregation on the surface of perovskite electrode(e.g. lanthanum strontium cobalt ferrite(LSCF)) and formation of an insulating secondary layer is dominant surface degradation mechanism.

In this research, the focus is on enhancing the performance and stabilization of LSCF air electrodes in rSOCs through ALD CeO₂, which is well known for its exceptional ionic conductivity and surface exchange activity. Its potential for enhancing the oxygen evolution reaction(OER) and oxygen reduction reaction (ORR) in rSOCs has been investigated. Electrochemical characterizations were carried out to compare bare LSCF(without ALD) with ALD CeO₂-coated electrodes. Interestingly, the initial electrochemical performance with ALD CeO₂-coated(10nm) sample showed 30% increase in maximum power density on SOFC mode and 10% increase in current density in SOEC mode. During long-term rSOCs operation at 750°c for over 100 hrs, the thermal stability of the ALD CeO₂-coated cell improved by 100% compared to the bare LSCF cell.

AA-TuP-93 Comparison of Thermal and Remote-Plasma ALD to Prepare Schottky Diodes to Gallium Nitride, *Suzanne Mohney, J. Clark, C. Chiu, T. Larrabee, N. Banner, N. Redwing, J. Gray,* Penn State University

We have explored the use of atomic layer deposition for creating Schottky diodes to *n*-type GaN, which is an important wide-bandgap semiconductor for power electronics. For high-temperature applications, we wanted to deposit a metallization that is unreactive with GaN. There are conductive metal nitride candidates in thermodynamic equilibrium with GaN, including Mo₂N, [1] but we did not want to prepare layers by sputter deposition due to electrically active defects that can be introduced in the GaN by the plasma. Instead, we prepared diodes using thermal ALD and compared them to diodes we reported previously using ALD with a remote plasma. [1] With bis(tertbutylimido)bis(dimethylamino)molybdenum as the precursor, the co-reactants were NH₃ or a remote N₂-H₂ plasma. Thermal ALD was performed with the stage at 250 °C and walls of a Lesker LX reactor at 200 °C using a stop-flow process, while the remote-plasma process was performed in a Veeco Gen II reactor at 200 °C. In both cases, the layers contained carbon, similar to other reports using this precursor, [2, 3] but fortunately Mo₂N can dissolve MoC, [1] and the films were good conductors. Thermal ALD resulted in diodes with a Schottky barrier height of 0.69 eV and an ideality factor of 1.06 before annealing, while the remote-plasma process created non-ideal diodes that initially exhibited high reverse currents. After annealing in N₂ at 600 °C, however, the diodes prepared by both methods offered similar Schottky barrier heights of 0.84 eV by thermal ALD and 0.87 eV by remote-plasma ALD. Moreover, the diodes prepared with the remote-plasma process were ideal after annealing. At room temperature, an ideality factor of 1.02 is expected due to image force lowering and was measured after annealing the diodes

prepared using the remote-plasma process. After annealing the diodes prepared by thermal ALD, the ideality factor became 1.04. Cross-sectional transmission electron microscopy suggests a very thin interfacial layer in the diodes prepared by thermal ALD, which may be the origin of the slight non-ideality after annealing. The authors gratefully acknowledge the support of ONR through N00014-22-1-2462 (Approved, DCN# 543-1698-24).

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AA-TuP-94 Y₂O₃ Thin Film Deposition Via Atomic Layer Deposition Utilizing Y(EtCp)2(iPr-amd)And O₃, *S. Cho, Seunghwa Choi,* Sungkyunkwan University (SKKU), Republic of Korea

These days there are many microstructures in semiconductor equipment. Especially equipment using plasma-enhanced deposition has narrow and complicated structure peripheral parts. These parts need to be stable with plasma damage. So, these parts need to be coated with material, which can protect the parts from plasma damage. Y2O3 is well-known for plasma passivation material. In this study, a study was conducted to coat Y2O3 thin films with atomic layer deposition (ALD) method for this purpose. Since the structure of the parts used in semiconductor processing equipment is becoming more complex, ALD is the most suitable method for uniformly coating parts that have complex structures. Y2O3 ALD thin films were deposited using Y(EtCp)2(iPr-amd) for Y precursor, and ozone for oxygen. The material characteristics and plasma stability of the deposited Y2O3 thin films were evaluated.

AA-TuP-95 Microstructure and Environmental Stability of Plasma-Enhanced ALD TiO₂/SiO₂ Multilayer Anti-Reflective Films on PMMA Substrates, *D. Cu, J. Ho,* Department of Optics and Photonics, National Central University, Taiwan; *W. Cho, C. Kei,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan; *Chien-Cheng Kuo,* Department of Optics and Photonics, National Central University, Taiwan

In this study, plasma-enhanced atomic layer deposition (PE-ALD) technology was used to coat an anti-reflective (AR) film on a PMMA substrate using TDMAT and 3DMAS precursors for TiO₂ and SiO₂ films, respectively, at a low temperature of 70°C. The plasma mode introduced a mix of oxygen and argon for oxidation. The refractive index (n) and extinction coefficient (k) trends in the single-layer film were examined to determine optimal process parameters and conditions. Due to the soft nature of the plastic substrate, a 50-watt setting was chosen for AR film deposition to avoid substrate surface damage and crack formation caused by ion bombardment at higher power settings.

The structures of single and multi-layer films were analyzed using various measurement instruments. X-ray diffraction confirmed the composition of the TiO₂ film structure, revealing an increase in crystallization strength from 82 to 117 as the number of ALD cycles (indicative of film thickness) increased from 200 to 1200. Atomic force microscopy showed a film surface roughness of approximately 0.28 nm, indicating a notably flat surface and a microcrystalline state for the single-layer TiO₂ film. Transmission electron microscopy verified that the multi-layer film structure matched the layer count predicted by Macleod simulation software.

Incorporating an inhibition layer within the nano-composite layer of a single film can effectively reduce the crystallization phenomenon and subsequently lower the stress on the film. The film's changes and durability under harsh conditions (85°C and 85% humidity) were observed using a constant temperature and humidity machine. AR films without the inhibition layer lasted up to 998 hours, while those with four inserted layers of 1.5nm SiO₂ only persisted for 209 hours. The results suggest that increasing the number of insertion layers does not significantly improve the stress on TiO₂. Instead, the thickness of TiO₂ decreases, causing the film to become less dense and more susceptible to erosion by moisture in high humidity conditions. In contrast, the relatively thicker TiO₂ film in non-inserted layers is denser, resulting in a lower water vapor transmission rate (WVTR) and better durability for the AR film.

AA-TuP-96 Optimization of Atomic Layer Deposition Process for Tin Oxide Thin Films at Low Deposition Temperatures for Halide Perovskite Solar Cells, *Saurabh Gupta, L. Laxmi, A. Paul, V. G. Chityala, S. Nayak, M. Misra, D. Kabra,* Indian Institute of Technology Bombay, India

Tin oxide (SnOₓ) thin film, having properties such as high transparency, conductivity, higher electron mobility, band alignment with halide perovskite materials, and high mass density has potential to be employed in

optoelectronic devices. Halide perovskite solar cells (PSCs) with high power conversion efficiency and low-cost of fabrication are promising candidates for next-generation tandem photovoltaics. However, tandem configuration requires to deposit sputtered transparent electrodes. This sputtering process damages the underneath organic and perovskite layers. Atomic layer deposited SnO_x thin film is capable to protect the damages and is compatible with electron transport layers for NIR-transparent PSCs. Thin films via Atomic Layer Deposition (ALD) process are pin-hole free, dense, uniform, conformal and deposited at lower temperatures. This study focuses on the optimization of ALD recipe parameters for the deposition of SnO_x thin films at low temperatures. This work investigates the effects of deposition temperature, precursor exposures, and purge times on the growth behaviors and on structural, optical, and electrical properties of SnO_x thin films. Our ~20 nm SnO_x films are having high average transmittance (>94.8 %), varied refractive index (1.78 to 1.95), negligible extinction coefficient, stoichiometric ratio of O/Sn (1.69 to 1.95), and mass density (>5.6 gm/cm^3) are suitable to be employed as functional layers in NIR-transparent PSCs. We successively applied the optimized SnO_x film in NIR-transparent PSCs as a protecting layer. We further explored annealing treatment of these films which enhances transmission (>95.6 %) and resistivity (min. 1.79E-2 Ohm-cm) properties. These enhanced-quality films show potential as other forms of functional layers in optoelectronic devices.

AA-TuP-97 Atomic Layer Deposition for Proton-exchange Membrane Water Electrolyzers, *Bhavesh Chavan*, *A. Tzavara Roussi, V. van Steijn, R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Proton-exchange membrane (PEM) water electrolyzers represent the forefront of hydrogen production through water electrolysis. However, they heavily rely on platinum group catalysts and titanium structures, which constitute a significant portion of the total electrolyzer costs *Babic et al.(2017)*. The emergence of atomic layer deposition (ALD) technology offers a promising solution to address these challenges by providing precise control over film thickness, maximal material utilization, and excellent conformality.

In this poster, we explore the versatile applications of ALD in both catalyst coated membrane (CCM) and porous transport electrode (PTE) configurations. In CCM, platinum group catalysts can be efficiently coated on carbon powder using fluidized bed reactor ALD (FBR-ALD) and subsequently applied to membranes *Lee et al.(2020)*. In PTE, ultrahigh mass activities are achieved by atomically depositing Pt and Ir nanoclusters on titanium and graphite felts for anode and cathode sides, respectively *Laube et al.(2021)*. Moreover, porous transport layers and bipolar plates, typically made from titanium and stainless steel, are coated with ultrafine Pt, Au, or nitride coatings to withstand high acidic and oxidation potentials *Woo-Lee et al.(2020)*. Additionally, ALD is explored for fabricating support materials and providing porous and protective coatings in the form of oxides and metal- organic frameworks (MOFs) and so on *Li et al.(2024); Xiao et al.(2024)*.

This poster will comprehensively discuss various literature studies and propose the best possible options for utilizing ALD in fabricating various electrolyzer components. Such advancements highlight the potential of ALD in revolutionizing the efficiency, cost-effectiveness, and durability of PEM water electrolyzers, thus paving the way for scalable hydrogen production with sustainability.

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AA-TuP-98 Mitigating Competing Reactions: Atomic Layer Deposition of Ultrathin Overlayers for Anode Protection in Direct Seawater Electrolysis, *Katherine Encalada*, *J. van Ommen, R. Kortlever,* Delft University of Technology, Netherlands

Direct seawater electrolysis is a promising technology for green hydrogen generation. Nonetheless, technical challenges arise due to seawater's complex chemical composition. Specifically in acidic media, the problematic competition at the anode between the undesired chlorine evolution reaction (CER) and the targeted oxygen evolution reaction (OER). Previous studies showed that permeable overlayers like MnOx and SiOx can selectively suppress the CER. However, the overlayer´s liquid deposition techniques resulted in non-uniform thickness and poor stability [1,2]. This work explores the effectiveness of an ALD-deposited SiO_2 overlayer on a GC-supported IrO_2 catalyst to suppress competing reactions at the anode during water electrolysis in an acidic chloride-containing electrolyte.

The methodology to quantify the competing OER vs. CER consists of a Rotating Ring Disk Electrode (RRDE) setup that simultaneously measures the oxidation (disk) and reduction (ring) currents within a potential range. Both competing reactions are promoted at the disk (IrO_2|GC) by sweeping the potential from 1,1 V to 1,55 V vs RHE. In this first step, water molecules and chloride ions oxidize, forming O_2(g) and Cl_2(g). The second simultaneous step involves reducing at the ring (Pt) the previously formed Cl_2(g), for which the ring is kept at 1,09V vs. RHE. This way, measuring how much Cl_2(g) evolved at the disk is possible. The SiO_2 overlayer was built by atmospheric ALD using $SiCl_4$ and water as reactants at 100 °C reaction temperature. Comparative measurements were conducted with and without the SiO_2 overlayer on the IrO_2|GC catalyst.

The preliminary results show that a thin layer of 25 cycles of SiO_2 by ALD gives a promising suppression of CER over OER. However, after subjecting the system to 20 cyclic voltammograms, the electrochemical behavior of the anode reverts to the one obtained with bare IrO_2. This observation suggests a SiO_2 overlayer's instability, presumably arising from a physical detachment of the overlayer from the substrate. Despite this setback, some strategies to improve the anchoring of the coating are to be yet explored, like pre-activation of the substrate or the usage of more reactive precursors like O_3.

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AA-TuP-99 Monolayer Engineering and Novel Annealing Techniques to Enhance the Ferroelectricity of HfO₂-Based Thin Films with a Low Thermal Budget, *Ting-Yun Wang*, *C. Mo, C. Chuang, Y. Yin, M. Chen,* National Taiwan University, Taiwan

HfO₂-based ferroelectric thin films have emerged as promising materials for a wide range of applications, including non-volatile memory and neuromorphic computing. Consequently, intensive research efforts have been made to develop and optimize various film compositions and processing techniques to enhance their ferroelectric properties. However, a notable challenge is the high annealing temperature requirement for HfO₂-based ferroelectric thin films, which conflicts with the low thermal budget constraints (<400ºC) of the back-end-of-line process in advanced semiconductor technology nodes. In this study, we present two novel approaches to overcome this limitation and enable pronounced ferroelectric performance of HfO₂-based thin films with a low thermal budget. The first approach introduces the concept of "monolayer engineering" by exploiting the layer-by-layer growth of atomic layer deposition (ALD). A significant remnant polarization ($2P_r$) ~ 30 $\mu C/cm^2$ was achieved in ~ 4 nm thick $Hf_{0.5}Zr_{0.5}O_2$ thin films by replacing the HfO_2 monolayer with the ZrO_2 monolayer in the vicinity of the bottom electrode. In particular, the sub-5 nm $Hf_{0.5}Zr_{0.5}O_2$ thin films exhibited pronounced ferroelectric behavior in their pristine state, even at the relatively low annealing temperature of 370ºC. This is noteworthy because it is typically difficult to achieve ferroelectricity in HfO₂-based thin films with thicknesses below 5 nm. This result highlights the distinguished capability of monolayer engineering to precisely tailor materials at the atomic scale, leading to exceptional functional properties in nanoscale ultrathin films. In addition, the second technique involves the development of "large-area electron beam annealing (EBA)" to obtain highly crystalline Al-doped HfO₂ (HAO) thin films deposited by ALD. The EBA treatment produces a highly localized annealing region within approximately 20 nm below the sample surface, which effectively mitigates the inherent thermal budget constraints imposed by the high annealing temperatures typically required for HAO thin films. As a result, an impressive ferroelectricity of $2P_r$ ~ 29 $\mu C/cm^2$ and high crystallinity of the orthorhombic phase were achieved in HAO thin

films by EBA with a low thermal budget. In summary, both techniques provide innovative ways to achieve significant ferroelectric performance of nanoscale HfO_2-based thin films with low thermal budgets.

AA-TuP-100 2D Transition Metal Chalcogenide Films Synthesized by ALD as Diffusion Barriers in Interconnects, *Sanne Deijkers*, H. Thepass, A. de Jong, Eindhoven University of Technology, The Netherlands; *H. Sprey, J. Maes,* ASM, Belgium; *E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

For the continuous miniaturization of nanoelectronics, the conventional TaN/Ta barrier, preventing Cu diffusion in interconnect structures, needs to be scaled down below the current thickness limit of 3 nm[1]. Replacing the conventional barrier with a two-dimensional transition metal chalcogenide (2D-TMC) offers the opportunity to reduce the thickness of the barrier. Atomic layer deposition (ALD) provides the conformality and suitable process temperatures required for back-end-of-line application of the 2D films. In this work we will demonstrate the performance of various 2D-TMCs synthesized by ALD as Cu diffusion barrier.

Previously, we showed that $ALD\text{-}MoS_{-2}$ of various thicknesses is an effective Cu diffusion barrier[2]. In addition, other 2D-TMCs deposited by ALD, such as WS_2, TaS_x and NbS_2, were tested by time-dependent dielectric breakdown measurements. These materials show differences in barrier performance. Highly crystalline MoS_2, specifically, showed superior blocking with respect to the other TMC films, as the median time to failure is $(3.2\pm0.1)\cdot10^3$ s for 2.2 nm MoS_2 versus $(5.3\pm0.1)\cdot10^2$ s for 10 nm TaS_2. All 2D-TMC films deposited by ALD result in relatively small grains (~10 nm)[3]. However, the degree of crystallinity differs per film as it is strongly affected by the process conditions, mainly by temperature and plasma composition (e.g., H_2S/H_2 flow ratio). Furthermore, some of the films show out-of-plane oriented growth besides the in-plane crystal growth, resulting in a mixed morphology. The combination of grain size, degree of crystallinity and morphology leads to different barrier performances, where a higher degree of crystallinity generally results in better Cu diffusion blocking.

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AA-TuP-101 Rational Design of a Full Plasma-Enhanced ALD Super-Cycle Process for Indium Gallium Zinc Oxide Based on in-Situ Characterization, *P. Plate,* Sentech Instruments GmbH, Germany; *C. Morales, A. Mahmoodinezhad,* BTU Cottbus, Germany; *L. Marth, Bodo Kalkofen,* Sentech Instruments GmbH, Germany; *M. Zoellner,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany; *K. Henkel, J. Flege,* BTU Cottbus, Germany

Transparent conducting oxides are a promising materials class for applications in the field of photovoltaics and thin film transistors. For the latter, indium gallium zinc oxide (IGZO) can be an enabler for the next generation of flexible electron devices and organic light-emitting diode displays due to its high optical transparency and electron mobility. In the past, IGZO was usually deposited by radio-frequency magnetron sputtering, solution processing, and pulsed laser deposition. More recently, atomic layer deposition (ALD) has shown the potential to overcome limitations of the other deposition methods allowing low-temperature processing and uniform depositions on 3D structures.

This work presents a bottom-up approach for the deposition of IGZO layers by a super-cycle ALD process using a SENTECH plasma-enhanced ALD (PEALD) reactor. Initially, a super cycle combining a thermal process (TALD) for zinc oxide (ZnO) and plasma-enhanced processes for gallium and indium oxide (Ga_2O_3, In_2O_3) was developed. The growth mechanisms of the individual processes within the super-cycle have been thoroughly investigated and monitored by in-situ ellipsometry (i-SE, SENTECH ALD Real-Time-Monitor). A nucleation delay for the thermal ZnO process was found, making it challenging to properly adjust the elemental composition by the sub-cycle ratio. Hence, the thermal ZnO cycle has been replaced by a plasma-enhanced ZnO process, which shows no nucleation delay, thus enabling a full PEALD super-cycle at low temperature (150°C).

X-ray photoelectron spectroscopy, grazing-incidence X-ray diffraction, and scanning electron microscopy in combination with energy-dispersive X-ray fluorescence analysis were used to investigate the elemental composition and morphology of the ALD films. Our results demonstrate that the elemental composition can indeed be precisely adjusted by varying the sub-cycle ratio within the super-cycle. Furthermore, metal/insulator/semiconductor (MIS) layer stacks were built to measure the electrical performance of the oxide films. This showed that the conductivity of films prepared using the full PEALD super-cycle is significantly higher than that of the layers deposited by the mixed TALD/PEALD process.

Therefore, this approach allows the preparation of ultra-thin IGZO layers with controlled thickness, composition, and electrical properties, while thermally induced segregation is largely prevented.

AA-TuP-102 Fabrication of ZnO Metal-Semiconductor-Metal Photodetectors on Cotton via Thermal-ALD, *H. Mousa, H. Saleh, L. Antoine, J. Goosen, F. Bayansal,* University of Connecticut; *M. Aboelkheir, T. Uyar,* Cornell University; *Ali K. Okyay,* OkyayTechALD, Turkey; *N. Biyikli,* University of Connecticut

Studies on electronic textiles have continued to increase in recent years and some applications have begun to find a place in daily life. Various flexible devices fabricated on textiles have been developed, including sensors, solar cells, and energy storage devices. In particular, wearable photodetectors (PDs) have attracted the attention of researchers due to their possible contributions to security, health, and communication applications. Zinc Oxide (ZnO) is one of the most suitable materials for textile-based PDs due to its wide bandgap, stability under long-term light exposure, and high sensitivity to UV/visible radiation. However, integrating thin film devices on textiles often affects their mechanical properties such as flexibility, durability, and washability. This work presents an approach that leverages low-temperature atomic layer deposition (ALD) of ZnO on cotton to achieve flexible PDs while preserving the inherent properties of cotton.

ZnO was deposited on cotton (woven bleached, 98 gsm) substrates using diethylzinc (DEZ) and H_2O as Zn precursor and co-reactant respectively in a thermal ALD reactor at 120 °C. The unit ALD cycle in which 20 sccm N_2 is used as the carrier gas consists of 0.5s DEZ pulse, 30s purge, 0.5s H_2O pulse, 30s purge steps. Following the deposition of ZnO layers on cotton, interdigitated electrodes consisting of 25/150 nm Ti/Al layers were evaporated by e-beam deposition to create the metal-semiconductor-metal (MSM) structures.

The resulting ZnO films on cotton are characterized in terms of their structural, morphological, compositional, and photo-response properties. X-ray diffraction analysis revealed the polycrystalline nature of the as-grown ZnO layer on cotton. SEM and EDX analyses showed that ZnO is uniformly synthesized on cotton. The photo-response characteristics of the fabricated MSM-PD device structures were examined by placing a visible light source at a distance of 30 mm. The bias voltage was scanned from –1 to 1V in a 50-mV step under dark and illuminated conditions. The resulting photo-current at 1V bias showed ~2.5-fold increase when compared to dark current (from 57 to 130 µA). Our study displays an effective ZnO-based photodetector on cotton at low bias voltages highlighting the potential for low-power wearable sensing applications. Future studies could focus on further characterizing the spectral photo-response under various environmental conditions and optimizing the device architecture by exploring different doping strategies, or composite structures that can enhance light absorption.

AA-TuP-103 Enhancing Charge Trapping Performance of Hafnia Thin Films by using Sequential Plasma Atomic Layer Deposition, *SoWon Kim, J. Yu, W. Park, H. Lee,* Tech University of Korea

HfO_2, as a high-k dielectric material, holds promise for replacing silicon nitride-based charge trapping layers (CTL) in traditional NAND flash memory. This is due to its high trap densities, significant conduction band offset with respect to the tunneling oxide (TO), and thin equivalent oxide thickness (EOT).

The Direct Plasma (DP) ALD process offers advantages such as higher film density and lower process temperatures compared to thermal ALD processes. However, because the plasma discharge happens within the chamber, it risks damaging the substrate through ion bombardment, potentially degrading device characteristics.

In Remote Plasma (RP) ALD, the plasma discharge occurs in a separate space, with thin film progress achieved by supplying radicals. However, it suffers from low productivity due to longer cycle times. By carefully considering the pros and cons of both plasmas, it is possible to mitigate device damage and cycle time simultaneously.

This study employed a Sequential Plasma ALD process to deposit HfO₂ films. Sequential RP and DP-ALD processes were utilized, allowing for thickness variation in each layer during deposition. Thin films of HfO₂ deposited by RP-ALD on the substrate ranged from 0 nm to 7 nm, forming a total of 10 nm HfO₂ thin films. Additionally, a Charge Trapping Memory (CTM) with an Au/Al₂O₃/HfO₂/SiO₂/p-Si (MAHOS) structure was fabricated using the deposited film to analyze RP-ALD thickness effects and assess memory operational characteristics degradation.

The HfO₂ film with a 4-nm-thick RP-ALD exhibited a significant memory window of over 7 V across a gate voltage range of ± 10 V, along with a relatively low interface trap site of $1.3×10^{12}$ $eV^{-1}cm^{-2}$ or less. As the thickness of the RP-ALD-deposited HfO₂ increased, both memory window and time-dependent dielectric breakdown (TDDB) endurance improved, while interface trap sites and V_{FB}(flat band voltage) shift with read/write repetition decreased.

In conclusion, the methodology proposed in this study is promising for future implementations of multi-level charge-storage nonvolatile memories or synaptic devices requiring numerous states.

AA-TuP-104 Atomic Layer Deposition of Self-Healing Protective Coatings for Stone Cultural Heritage Conservation, *Aranzazu Sierra Fernández,* CIC nanoGUNE, Donostia-San Sebastián, Spain*; M. Knez,* CIC nanoGUNE, Donostia-San Sebastián and IKERBASQUE, Basque Foundation for Science, Spain

The development of protective coatings for the construction industry and cultural heritage (CH) applications with combined strength, toughness, and compatibility remains a long-standing challenge. Applying a hybrid coating system to building components before the onset of severe damage could effectively increase longevity and reduce maintenance demand. This study introduces a novel self-healing coating, deposited via Atomic Layer Deposition (ALD), to advance the protection of porous stone substrates. The ALD layers incorporated metal oxides that trigger a self-healing mechanism, including passivation processes aimed at autonomously repairing micro-damages, thusextending the durability of the material.The ALD process was precisely tailored to facilitate the formation of metaloxide interfaces,whichwere key to the self-healing functionality. A comprehensive evaluation of their mechanical properties on stone substrates is presented to validate the self-healing capabilities of the coatings after exposure to simulated environmental conditions such as variations in relative humidity, temperature, and UV light. This characterization approach involved both nanoindentation, assessing the hardness and elastic modulus at the nanoscale, and microindentation, determining the mechanical integrity at a larger scale. This method enabled us to capture the responses of the coatings to external mechanical stimuli across different scales, thereby providing detailed insights into the effectiveness of the self-healing process. Preliminary results indicate a promising enhancement in the resistance of the coatings to mechanical stresses and microfracture propagation. Through meticulous design and characterization, this research endeavors to develop a self-healing coating system that not only protects, but actively maintains the integrity of CH stone materials. The implementation of such technology stands to redefine conservation methodologies, offering a sustainable and efficient approach to CH preservation.

Area Selective ALD
Room Hall 3 - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Selective Metal Blocking using Vapor-Phase Self-Assembled Monolayers for Area-Selective Atomic Layer Deposition of Dielectrics*, Jeong-Min Lee, W. Kim,* Hanyang University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) offers complementary bottom-up patterning with atomic-level accuracy on pre-defined areas in conjunction with conventional top-down patterning, so it has attracted tremendous interest for enablement of multi-dimensional nanostructures toward sub-10 nm scale technology. In this study, we report a methodology for achieving selective deposition of dielectric thin films by using vapor-phase self-assembled monolayers (SAMs) accompanied by post-surface treatment. First, we investigated the AS-ALD of ZrO₂ films for dielectric versus metal selectivity through vapor-phase phosphonic acid (PA) SAMs treatment with long alkyl chains. The blocking capability of PA SAMs was comparatively evaluated with O₃ and O₂ reactants on SiO₂, TiN, and W substrates, and we confirmed that a relatively high deposition selectivity above 0.9 can be achieved even after ALD 200 cycles with mild oxidizing

reactant. Further, electrical properties of ZrO₂ films deposited with both reactants were also investigated comparatively with and without post-surface treatment, and as a result, it was demonstrated that high-quality ZrO₂ films with high dielectric constant can be fabricated through the post-surface treatment. Second, we confirmed the AS-ALD of SiO₂ films only on SiO₂ substrates through vapor-phase functionalization of PA SAMs with fluoroalkyl chains. By using the mild oxidant in subsequent ALD process, selective deposition of SiO₂ thin films over ~8 nm on SiO₂ versus TiN and W substrates was successfully demonstrated.We anticipate that this work provides a new strategy to achieve highly selective deposition for AS-ALD of dielectric on dielectric (DoD) application toward the upcoming bottom-up 3D nanofabrication.

AS-TuP-2 Area-Selective ALD of Transparent Conductive Oxides by Using Polymer Patterns Generated with High-Precision Capillary Printing*, Ludovic Hahn,* CEA-LETI, France*; M. Pascual, A. Guitton, K. Farmand, A. M'Barki,* Hummink, France*; T. Jullien, L. Golanski, C. Guerin, V. Jousseaume,* CEA-LETI, France

Transparent conductive oxide thin films are widely developed for numerous applications in optoelectronics due to their unique properties. However, the oxide film needs to undergo patterning, which is often difficult to achieve with standard lithographic steps. Indeed, those materials are difficult to integrate due to their sensitivity to chemistry, like ZnO, which is water-sensitive. This problem becomes even more dominant when reducing the features for further application. An alternative to photolithographic steps is Area Selective Deposition (ASD), which uses an inhibiting layer such as a polymeric film that prevents oxide deposition on certain controlled regions.

In this work, polymeric films were printed by an innovative direct nanoprinting technique [1]. This High Precision Capillary Printing (HPCAP) technique is based on AFM technologies. A nanopipette filled with the ink of interest will oscillate at a high frequency and deposit the ink to form complex geometries at the surface of a substrate. A precision of 20 nm in the xy plane and a resolution between 100 nm and tens of microns can be achieved, which, coupled with a high deposition rate, makes it a good alternative for additive manufacturing.

Micrometric patterns of polymers, comprising poly(methyl methacrylate) (PMMA), poly(vinyl pyrrolidone) (PVP) and an epoxy-based resist (SU-8) were drawn on silicon substrate. Then TCO, such as ZnO and SnO2, were deposited on the patterned polymers by low-temperature ALD. By using spectroscopic ellipsometry, atomic force microscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy, it is shown that PMMA inhibits both oxides, compared to PVP and SU-8, which only suppress ZnO growth. Moreover, an exclusion zone around the polymer pattern where oxides are inhibited is observed, depending on the polymer used. The study of the impact of the pattern size (from a few μm to a few tens of μm) reveals that this exclusion zone is independent of the geometry but mainly depends on the polymer used and the type of oxide deposited.

Finally, the polymers can be selectively removed leading to a selective deposition of TCO and a 10 μm pixel array was successfully produced. This original approach combining the direct nanoprinting of a polymer pattern with the subsequent ALD deposition of TCO appears to be a promising path for the patterning of a sub-10 μm matrix of pixels.

[1] M. Pascual, N. Bigan, A. M'Barki, R. Mental, I. Allegro, U. Lemmer, SPIE Opto 2023, 124330E

AS-TuP-3 Photo-Enhanced Selective Area Atomic Layer Deposition*, Paul Butler,* Walter Schottky Institut, Technische Universität München, Germany*; L. Sortino,* Ludwig-Maximilians-University of Munich, Germany*; S. Maier,* Monash University, Australia*; I. Sharp,* Walter Schottky Institut, Technische Universität München, Germany

One of the major challenges that ALD currently faces is the lack of lateral control, which has led to an ongoing interest in selective-area ALD (SA-ALD) techniques that can allow for bottom-up fabrication of micro- and nano-structures. In this respect, photo-enhanced ALD (photo-ALD), in which well-defined photoexcitation is used to activate chemical reactions at certain areas on a surface, holds significant promise for SA-ALD. However, relatively few studies on photo-ALD have been conducted and the spatial resolution of this technique remains limited. Here, we present a novel approach to achieving SA-ALD via *in situ* photoexcitation of the surface. Our experiments demonstrate that optical laser excitation enhances ALD-growth of TiO₂ films on gold substrates, with the deposition rate increasing with laser intensity. To investigate the photo-induced reaction, gold-coated silicon substrates were sequentially exposed to titanium isopropoxide (TTIP)

and ozone outside the normal ALD process window, with some substrates exposed to illumination from a 515 nm laser. Using *in situ* spectroscopic ellipsometry to monitor the growth rate of the TiO_2 films during the ALD deposition, we find an illumination-activated growth that can be assigned to enhanced oxidation of the adsorbed precursor. Furthermore, patterned illumination through a shadow mask results in laterally structured growth, as verified by ex situ ellipsometry mapping. Ongoing work is now devoted to identifying thermal and electronic contributions to the growth mechanism, as well as coupling the exciting illumination to plasmonic gold nanostructures. Overall, this method of selective-area photo-ALD could later be applicable to bottom-up nanofabrication, with applications ranging from nanoscale optoelectronics to photocatalysis.

AS-TuP-4 Area-Selective Atomic Layer Deposition of Bilayer Materials Using Polymethylmethacrylate Thin Films as Blocking Layers, *Aditya Chalishazar, N. Poonkottil, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Area-selective ALD (AS-ALD) is an interesting subset of ALD where materials are selectively grown on specific areas of the substrate. As an additive bottom-up approach, it has immense potential for reducing the number of steps in nanomanufacturing [1-3].

AS-ALD studies have mostly been limited to single-material deposition. Multi-material AS-ALD poses additional challenges as it requires the ALD process chemistries to be compatible in their temperature windows and chemical selectivity. Realizing multi-material ASD has become an interesting challenge in recent years [2,4]. In particular, selective deposition of multilayers can substantially reduce processing time for the fabrication of nanoscale devices.

In this work, we explore the use of metal dialkylamide precursors with polymethylmethacrylate (PMMA) masking layers to realise multi-material AS-ALD. PMMA is a popular AS-ALD inhibitor layer: it can be patterned using various approaches and can easily be removed using exposure to plasma or dissolution in appropriate solvents [3,5].

Here, ALD of SnO_2 and Ta_2O_5 using their dialkylamide precursors and water at 120 °C was performed on Si and blanket PMMA substrates. Selective deposition of SnO_2 and Ta_2O_5 is obtained on Si with negligible deposition on the PMMA blanket substrate after 100 cycles (Figure 1), which was confirmed by XRR/XRF and XPS measurements. SnO_2 was then deposited on a PMMA patterned wafer and studied using energy dispersive X-ray spectroscopy (EDS), which showed deposition between the PMMA pattern (Figure 2a-c). The films were imaged after plasma treatment, which resulted in a SnO_2 pattern (Figure 2d-f). Extending this concept, we deposited a SnO_2-Ta_2O_5 bilayer using a PMMA masking pattern, followed by mask removal with oxygen plasma (Figure 3). This demonstrates the deposition of a multilayer material using one template material without the need for intermediate processing steps. We believe such a combinatorial approach using metal dialkylamide precursors and PMMA can open new avenues to the deposition of patterned multilayer devices for device manufacturing using AS-ALD.

[1] *Chemistry of Materials,* 2018, *31,* 2-12
[2] *Chemistry of Materials,* **2023,** *35,* 4375-4384
[3] *Advanced Materials Interfaces,* 2023, *10,* 2201934
[4] *ACS Nano,* **2021,** *15,* 12276-12285
[5] *Chemistry of Materials,* **2020,** *32,* 4920-4953

AS-TuP-5 Density Functional Theory Study on Selective Silylation of SiO_2 Against Cu Using Dimethylaminotrimethylsilane, *Misoo Kim, K. Khumaini, R. Hidayat, H. Kim, W. Lee,* Sejong University, Republic of Korea

Selective cobalt capping of the copper surface has been introduced to improve the electromigration resistance of copper interconnects. Chemical vapor deposition of cobalt on copper is inherently selective against silicon oxide, and the selectivity can be enhanced by silylation of the oxide surface to form an alkyl-terminated surface. In the previous work, we studied the selective chemisorption of the cobalt precursor on copper and showed that chemisorption is favored on copper but not on silicon oxide. We also showed that physisorption and chemisorption of the cobalt precursor are more difficult on alkyl-terminated SiO_2 than on OH-terminated SiO_2 [1]. Recently, another research group demonstrated that the alkyl-terminated surface is also essential for the selective atomic layer deposition of ruthenium films [2]. They observed that at 250°C, dimethylaminotrimethylsilane (DMATMS) readily reacts with surface –OH groups on SiO_2 to form –O–$Si(CH_3)_3$ groups. However, the theoretical study

of the reaction mechanism to form an alkyl-terminated silicon dioxide surface is rare. In addition, the reaction of DMATMS with metallic surfaces has not been reported by either experimental or theoretical studies. In the present work, we performed density functional theory (DFT) calculations to study the reaction mechanism for the selective silylation of DMATMS on silicon oxide against copper surfaces. We constructed two substrates, vicinal OH-terminated SiO_2 and bare copper substrate. All possible chemisorption pathways were considered. The reaction and activation energies of chemisorption on these two surfaces were calculated and compared. In addition, the Gibbs free energy changes for silylation were determined to explain the selective silylation at process temperature. The results can provide fundamental insights into the selective surface inhibition mechanism for area-selective deposition.

AS-TuP-6 Self-Aligned Patterning of Tantalum Oxide on Cu/SiO_2 with Inherent Selective Atomic Layer Deposition, *Kun Cao, Z. Qi,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; B. Shan,* State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

The chemical principal and mechanisms that enable selective atomic layer depositions are gaining rapid growing interests, which have unlocked attractive avenues for the development of novel nanostructures by depositing atoms at desired surface locations. In this talk, the inherently selective atomic layer deposition processes will be discussed. Tantalum oxide was studied on a series of oxide substrates. Although the oxides have -OH groups on the surface and proposed to have similar nucleation sites, there are long nucleation delays on basic oxides. The H-transfer reaction is a key factor to influence the reaction barrier. It is hard to nucleate on basic substrates because the H-transfer reaction is blocked. Another demonstration is the redox-coupled inherently selective ALD for self-alignment of tantalum oxide on SiO_2/Cu nanopatterns. By adding an in-situ ethanol reduction pulse before each traditional binary ALD cycle, and the 'reduction-adsorption-oxidation' ALD process increases the selectivity. Self-aligned manufacturing on nanoscale Cu/SiO_2 patterns without excessive mushroom growth at the edge and undesired nucleation defects on the Cu region. The process can be reliably repeated to yield more than 5 nm-thick Ta_2O_5 on the SiO_2 region, while no undesired deposition occurs on Cu patterns. In addition, an anisotropic growth model with the dynamical competition of expansion and dissociation of the nucleus is proposed to nucleation delay are quantitively predicted and the model provides a practical method to evaluate the selectivity of ALD theoretically.

AS-TuP-8 What Happens to Small Molecule Inhibitors after the Selectivity Is Lost: 4-Fluorophenylboronic Acid Functionalization of Silicon Surface to Inhibit TiO_2 Deposition, *Andrew Teplyakov, D. Silva-Quinones, J. Mason, R. Norden,* University of Delaware

As the size of the components in electronic devices decreases, new approaches and chemical modification schemes are needed to produce nanometer-size features with bottom-up manufacturing. Organic monolayers can be used as effective resists to block the growth of materials on non-growth substrates in area-selective deposition methods. However, choosing the appropriate surface modification requires knowledge of the corresponding chemistry and also a detailed investigation of the behavior of the functionalized surface in realistic deposition schemes. The 4-fluorophenylboronic acid (FPBA) can be used as a model to investigate the possibility to utilize the Si(100) surface functionalized with this compound as a non-growth substrate in a titanium dioxide (TiO_2) deposition scheme based on sequential doses of tetrakis(dimethylamido)titanium (TDMAT) and water and to follow what happens at the interface when the selectivity is eventually lost. A combination of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) allows for a better understanding of the process. The functionalized surface is shown to be as effective non-growth area to TiO_2 deposition when compared to currently used H-terminated silicon surfaces but to exhibit much higher stability in ambient conditions. Thermal treatment and analysis of F and B

labels allow for investigating interface stability and opportunities to use the scheme for monolayer doping.

AS-TuP-9 Modelling the Reactivity of Small Molecule Inhibitors by Density Functional Theory, *Fabian Pieck, R. Tonner-Zech,* Wilhelm-Ostwald Institut for Physical and Theoretical Chemistry, Leipzig University, Germany

Within area-selective atomic layer deposition selectivity is achieved by various approaches. We follow the strategy to block growth on the non-growth surface by the deposition of small molecule inhibitors (SMIs) prior to the atomic layer deposition (ALD) process. Here, the selectivity of the process can be improved by understanding the properties and reactivity of the SMIs at an atomic level. Especially, tuning the SMIs with respect to the studied surface and ALD process based on their blocking mechanism is highly valuable. To understand the impact of the SMI structure on its reactivity we are studying two classes of SMIs namely sulfur-based SMIs as diethyl sulfide[1], dipropyl sulfide and diisopropyl sulfide as well as nitrogen-based SMIs as aniline, pyridine and pyrrole (Figure 1). With SiO_2, Cu(111) and CuO(111) common metal and oxide surfaces are considered as substrate while these classes of SMIs are experimentally investigated for the deposition of HfO_2 and Al_2O_3, respectively.

We use ab initio modelling by density functional theory (DFT) to explore adsorption properties and on-surface reactivity of SMIs. Here, adsorption energies are used to find the most stable adsorption structures, while changes in the adsorption energies for multiple adsorbates help to identify ideal inter-molecular spacing and SMI packing density. Reaction paths and transition states are obtained by the nudged elastic band method while obtained activation energies reveal the most likely reactions. In addition, kinetic Monte Carlo (kMC) simulations are used to clarify the impact of obtained intermediates and side reactions on the desired product formation.

1. S. Zoha, F. Pieck, B. Gu, R. Tonner-Zech, H.-B.-R. Lee, Organosulfide Inhibitor Instigated Passivation of Multiple Substrates for Area-Selective Atomic Layer Deposition of HfO_2. *Chem. Mater.* 2024 accepted.

AS-TuP-12 The Formation of a Bottomless ZnO Barrier Using Inherent ZnO AS-ALD Process for Advanced Metallization, *Yuki Mori,* TANAKA Precious Metals, Japan*; Y. Son,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; S. Kim,* Ulsan National Institute of Scienece and Technology (UNIST), Republic of Korea*; S. Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Area selective atomic layer deposition (AS-ALD) is one of the most promising technologies for next-generation interconnect. The bottomless barrier using AS-ALD can reduce interconnect resistance by the deposition of barrier material only on the via sidewall (such as SiO_2/low-k) not on the via bottom (such as metal). Generally, in the previous studies, barrier materials are selectively deposited using long-chain inhibitors. Therefore, it is difficult to apply it to fine structures. Inhibitor-free inherent AS-ALD is a promising process to solve this problem. ZnO has been reported as the bottomless barrier of Cu interconnects by AS-ALD using an alkanethiol inhibitor [1]. There are many reports regarding AS-ALD of ZnO using inhibitors but the investigation on inherent inhibitor-free AS-ALD of ZnO is very limited [2] thought inhibitor-free ALD has clear advantages with device scaling-down. In this report, systematic studies on the inherent ZnO AS-ALD with substrate materials and process of substrate materials are described. Here, ALD of ZnO was basically conducted at 120 ºC by using diethylzinc (DEZ) and H_2O as a precursor and a reactant, respectively. DEZ and H_2O pulsing time were 1 second, where it guarantees the self-limited growth of ZnO. The results shows that there is no incubation cycle on SiO_2, but ~80 incubation cycle on H-terminated (Si-H). It indicates that the surface OH-groups on SiO_2 promote the adsorption of the Zn precursor, and the surface H-groups on Si-H prevent the adsorption of the Zn precursor. We also investigated about ZnO ALD on different metal surfaces and found that ALD-ZnO process shows a nucleation delay on clean metal surfaces with fewer surface OH-groups. On the easily oxidized metals (such as Ti and Cu), ALD-ZnO process shows almost no incubation cycle. The present findings are expected to enable the formation of bottomless ZnO barrier without providing any inhibitor and reduce interconnect resistance in semiconductor devices.

[1] Y. Mori et al., Small **2023**, 19, 2300290.

[2] A. Mameli et al., Chem. Mater. **2019**, 31, 1250.

AS-TuP-13 Area-Selective Atomic Layer Deposition by Sputter Yield Amplification on Heavy Elements, *Arthur de Jong, M. Bär, M. Merkx, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) is an emerging approach for device fabrication, that can circumvent the need for lithography for specific layers in a device stack. The selectivity between the growth and the non-growth area is typically achieved on the basis of a chemical difference, by e.g. selective precursor or inhibitor adsorption [1]. To expand the ASD toolbox, a physical approach combining a non-selective ALD process with area-selective sputter etching by ions is investigated in this work. The advantage of sputter etching is its relative independence on temperature and ALD chemistry. To enable selective etching based on sputter yield amplification, the non-growth area requires an element with a much larger mass than the incoming ion [2]. The ions generated by a plasma arrive at the surface with an inwards facing momentum. If an ion collides with an atom having a much larger mass, this momentum is redirected upwards more efficiently as compared to a collision with a light atom. This efficient redirection increases the amount of energy that is transferred to surface atoms, resulting in a larger probability to etch them. The growth area should not contain heavy elements, leading to a much smaller etch rate.

To investigate the selective sputter etching, a thin SiO_2 overlayer deposited by ALD was exposed to low-energy Ar ions. The amount of SiO_2 removed depends significantly on the substrate material underneath (Al_2O_3, TiO_2, Nb_2O_5, MoO_3, HfO_2, Ta_2O_5 and WO_3 are investigated here). In general, the heavier the mass of the metal atoms in the substrate, the less SiO_2 is observed after the ion exposure. As demonstration for the feasibility of the approach, SiO_2 was selectively deposited on Al_2O_3 with respect to a HfO_2 non-growth area. The ASD process consists of repeating supercycles of three SiO_2 ALD cycles and Ar ion exposures from a plasma. Approximately 1.2 nm of selective growth is achieved on the Al_2O_3, while most deposition is effectively removed from the HfO_2 (<0.3 nm is observed). It is challenging to maintain the etch selectivity for thicker SiO_2 which can be mitigated by tuning the ALD process. This proof-of-concept shows that exploiting sputter yield amplification can enable ASD processes that are complementary to the existing chemical approaches.

[1]Mackus *et al.* (2019) Chemistry of Materials **31**, 2

[2]Berg *et al.* (1992) Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **10**, 1592

AS-TuP-14 Theoretical Investigation on Impurity Formation Mechanism During Area-Selective Atomic Layer Deposition Using Organic Inhibitors, *Jiwon Kim, B. Shong,* Hongik University, Republic of Korea

Recent advancements in semiconductor devices aim for performance improvement through miniaturization and also employing of three-dimensional architectures. Atomic layer deposition (ALD) is often employed for its advantages of high uniformity and conformality of the deposited thin films. Area-selective ALD (AS-ALD), a potential bottom-up approach for self-aligned fabrication of thin films, may offer process innovations that can solve fabrication challenges. Furthermore, ALD on high aspect ratio (HAR) substrates often involves challenge in conformality. It was recently shown that spatial modulation of the ALD growth rates by adsorption of inhibitors with gradient in density can enhance the conformality within the HAR structures. However, in such AS-ALD approaches, molecular inhibitors are often utilized to selectively deactivate the growth of thin films, which may result in increased impurity levels if unwanted side reactions occur. In this study, possible side reactions during AS-ALD of silicon nitride (SiNx) using organic small molecule inhibitors (SMIs) are investigated utilizing density functional theory (DFT) calculations. Complete removal of surface passivation group through reaction with the reactants is crucial for the deposition of thin films without carbon impurities. However, nitride materials such as SiNx often require high process temperature for thermal ALD, at which decomposition of precursors or inhibitors can occur. Then, the highly reactive chemical species resulting from the thermal decomposition can result in non-selective deposition regardless of surface inhibition. Furthermore, such reaction can result in formation of carbon-containing surface moieties that are significantly stable and resistant against removal, possibly leading to increased amount of carbon impurities. Therefore, our study suggest that the side reactions should be carefully considered for AS-ALD using SMIs.

AS-TuP-16 Effect of N2 Co-Flow During Area-Selective Atomic-Layer-Deposition of Al₂O₃, *Sangjun Lee*, Sungkyunkwan University (SKKU), Republic of Korea; *C. Park, Y. Choi, S. Jeong, S. Hong,* Sungkyunkwan University, Republic of Korea; *Y. Cho, H. Lee, H. Kim, A. Klipp,* BASF, Republic of Korea; *P. Yoo,* Sungkyunkwan University, Republic of Korea; *H. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

In semiconductor device manufacturing, accurate alignment of fine patterns is crucial for optimizing the chip's overall performance. Edge placement error (EPE), which occurs during the via forming process in back-end-of-line metal wiring, leads to increased parasitic capacitance and degrading the reliability and performance of the device [1, 2]. To address this issue, area-selective deposition of dielectric films emerges as a possible solution. This technique selectively elevates the interlayer dielectric or intermetal dielectric between neighboring metal lines, thereby minimizing potential conductive paths and effectively reducing RC delays [3].

In this study, we enhanced the selectivity of Al2O3 atomic layer deposition (ALD) on dodecylphosphonic acid-treated Cu substrates by co-flowing N2 during Al-precursor (trimethylaluminum) injection. The selectivity significantly increased as the N2 flow rate was increased from zero to 200 sccm, prompting the utilization of various characterization techniques to determine the origin. Contact angle measurements were taken to compare the blocking capability of the self-assembled monolayer when exposed to both the precursor and N2. The selectivity was evaluated by X-ray florescence and X-ray photoelectron spectroscopy analyses. Additionally, possible changes in the dielectric constant of the Al2O3 film were examined by electrically characterizing the capacitors fabricated with Al2O3 films deposited using various N2 co-flow rates.

[1] J. Mulkens et al., Proc. SPIE 10145, 1014505 (2017).

[2] A. T. Ngo et al., IEEE Trans. Semicond. Manuf. 36, 1 (2023)

[3] G. N. Parsons et al., J. Vac. Sci. Technol. A 37, 020911 (2019)

Emerging Materials
Room Hall 3 - Session EM-TuP

Emerging Materials Poster Session

EM-TuP-1 Atomic Layer Memory Switching for Power-Efficient Neuromorphic Computing, *Hyunho Seok*, S. Son, T. Kim, Sungkyunkwan University, Republic of Korea

Brain-inspired parallel computing has been considered for the breakthrough of memory bottlenecks to meet the needs of simultaneously overflowing informative data. Numerous studies have been conducted on the development of reliable memristor arrays, energy-efficient computing, and various operational mechanisms for synaptic devices. However, for bioplausible neuromorphic computing, and temporal and spatial investigations as input signals toward leaky integrate-and-fire systems should be realized.

In this research, the importance of two-dimensioinal material based neuromorphic computing is addressed, and the basic components of the hardware neural network system are presented. Transition metal dichalcogenides (TMDCs) which is widely utilized for advanced van der Waals (vdW) based electronics is proper candidate for neuromorphic devices owing to atomically thin layered structure and superior electronic properties. Owing to the atomic structures, low-powered energy consumption can be realized.

Two-terminal devices of artificial and artificial synapses have been used as single components in neuromorphic computing, but they are associated with critical issues, such as current leakage and the absence of a third terminal as a fine synaptic weight modulator. To fully mimic biorealistic artificial neural networks, the integration of artificial neurons and synapses, hardware implementation of neurobiological functionality, and sensory neuromorphic computing are required. From single-component devices to architectures, the operational mechanism of each artificial component is unraveled, and the realization of bioplausible neuromorphic computing through integration is comprehensively discussed for future brain-inspired electronic systems.

EM-TuP-2 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of TiCN Ternary Nitrides with Tunable Composition, Z. Sobell, **Michael Collings**, S. George, University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiCN ternary nitride films with tunable composition at T< 140°C.TiCN EE-ALD was performed using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) and electrons together with the continuous presence of an ammonia (NH₃) reactive background gas (RBG) (Figure 1). The electrons can remove surface species via electron stimulated desorption (ESD).NH₃ can also be dissociated by the electron beam to produce H and NH$_x$ radicals. The NH$_x$ radicals may facilitate Ti nitridation and C removal from the film (Figure 2). The C content of the TiCN films can be tuned by varying the electron beam exposure time or the NH₃ RBG pressure.

Reducing the electron beam exposure reduces the production of active NH$_x$ species and allows more carbon incorporation into the films during TiCN EE-ALD.Electron exposures were varied from 0.5 to 20 seconds. Electron exposures of 0.5 s resulted in a C:Ti ratio of 1:4, while electron exposures of 20 s resulted in a C:Ti ratio of 1:28, as measured by ex situ XPS (Figure 3).The resistivity of the films determined by 4-wavelength in situ ellipsometry is also affected by the carbon content.Films grown with a 0.5 s electron exposure had a resistivity of ~800 μΩ cm.Films deposited with a 20 s electron exposure time had a resistivity of ~200 μΩ cm.

TiCN films can also be grown by reducing the NH₃ partial pressure during TiCN EE-ALD.Lower NH₃ partial pressures lead to fewer active NH$_x$ species present in the reactor and allow for the incorporation of more C into the films. NH₃ pressures were varied from 0 to 3.3 mTorr.Both the C:Ti ratio and the resistivity of the films varied with NH₃ pressure.The C:Ti ratio varied from 2:1 at no NH₃ to 1:10 at 3.3 mTorr NH₃, as measured by ex situ XPS.The resistivity varied from ~1000 μΩ cm for no NH₃ pressure to ~200 μΩ cm at an NH₃ pressure of 3.3 mTorr.

The use of a RBG during EE-ALD allows for compositional tuning of thin films.For example, TiN or TiO₂ films can be grown using TDMAT together with either NH₃ or O₂ RBGs.Varying the electron exposure or RBG pressure can also be utilized to control the film composition.Growth of binary or ternary ALD films is straightforward because EE-ALD with RBGs relies only on simple, volatile, gas phase precursors.

EM-TuP-3 Low-Temperature Atomic-Molecular Layer Deposition of Air-Stable and Conformal Zn-Benzenedithiol Thin Films, *Anish Philip*, T. Jussila, Aalto University, Finland; *J. Obenlueneschloss, D. Zanders, F. Preischel,* Ruhr University Bochum, Germany; *J. Kinnunen,* Chipmetrics Ltd, Finland; *A. Devi,* Ruhr University Bochum, Germany; *M. Karppinen,* Aalto University, Finland

The atomic/molecular layer deposition (ALD/MLD) thin-film technique is strongly emerging as a unique designer's tool for exciting new functional metal-organic materials. Current research demonstrates that this method is effective even at low deposition temperatures and capable of producing thin films that are highly stable and conformal. Stability and conformality are critical requirements of today's 3D microelectronics and open vast potential for various industrial applications. In this context, we highlight the attractive characteristics of a new ALD/MLD process developed for Zn-organic thin films based on non-pyrophoric bis-3-(*N,N*-dimethylamino)propyl zinc [Zn(DMP)₂] and 1,4-benzene dithiol (BDT) precursors. This process yields air-stable Zn-BDT films with a notable growth rate of 4.5 Å/cycle at 60 °C. The reported process ability to produce highly conformal thin films was verified on lateral high-aspect-ratio (LHAR) test substrates.The Zn/S ratio (0.5) determined with RBS for a planar film was in alignment with the expected compositions. The depth-profile XPS analysis for a LHAR grown Zn-BDT film indicated a composition change along the cavity, which maybe arising from the different sticking coefficients of the precursors. The reported films were found to be electrically insulating and demonstrated remarkable stability under ambient conditions over extended storage periods, making them a promising candidate for barrier coating application in microelectronics. Also importantly, using state-of-the-art LHAR test structures we could demonstrate that by increasing the precursor pulse lengths it was possible to extend the essentially ideal film growth deep (PD=260 μm) into the high-aspect-ratio cavities (Figure 1).

EM-TuP-4 Tin Oxide-Organic Superlattices for Flexible Thermoelectric Applications by Atomic/Molecular Layer Deposition, *Mari Heikkinen,* Aalto University, Finland; *N. Huster, A. Devi,* Ruhr-University Bochum, Germany; *M. Karppinen,* Aalto University, Finland

Flexible thermoelectric (TE) heat-to-electricity conversion devices would be highly beneficial for wearable applications and also for any application in which the heat source is complex shape.[1] A TE device principle is simple, but it needs both n- and p-type semiconductor legs to function.

An efficient TE material should have simultaneously high electrical conductivity and low thermal conductivity, which is a challenge for conventional materials. The second challenge is that the currently

employed inorganic TE materials are composed of heavy/rare/poisonous elements (Bi, Te, etc.), which are not environmentally sustainable. Simple metal oxides like ZnO are relevant material candidates, but their thermal conductivity is too high.

The combined atomic and molecular layer deposition (ALD/MLD) technique allows us to mix inorganic and organic precursor pulses in a sequential manner, thus enabling precise layer-engineered superlattice (SL) structures. In our previous works, we have deposited ZnO:organic SLs where monomolecular organic layers are embedded within nanoscale layers of the n-type ZnO semiconductor to block the phonon conduction at the resultant metal oxide/organic interfaces without affecting the electrical conductivity.[2] Organic layers also improve the flexibility of the film.

Here we present similar efforts for the yet-missing p-type semiconductor counterpart SnO. We use an amidinate-based tin(II) precursor which reacts well with water as the co-reactant under ALD conditions for the deposition of the SnO layers.[3] Thin films deposited at 220 °C results in phase pure SnO. Saturation for tin precursor happens at 12 s and for water at 2 s. The thickness of the films is measured by X-ray reflectivity (XRR) and the composition analyzed by Fourier-transform infrared spectroscopy (FTIR). For the organic component, we investigate various possibilities (hydroquinone, terephthalic acid, etc.); tentatively, terephthalic acid is found a promising organic component, as it has more oxidative character than e.g. hydroquinone.

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EM-TuP-5 Low Temperature Plasma Synthesis of Layer controlled MoS$_2$ for Flexible AI Accelerator, *Sihoon Son*, H. Seok, D. Lee, H. Choi, T. Kim, Sungkyunkwan University (SKKU), Republic of Korea

The achievements in implementing flexible electronics, departing from rigid silicon-based hardware substrates, are accelerating the emergence of "electronic skin." Such flexible electronics are gaining attention as an attachable electronic augmentation ranging from patch-type medical diagnostic applications to, ultimately, enhanced replacement for actual skin.

The information processing in actual human skin entails a system that dynamically integrates sensory compliance, threshold adjustment, and other complex nervous system functions, rather than being a mere collection of simple sensors. To attach AI diagnostic systems to the skin or, further, to mimic such systems for electronic skin, it is essential to produce neuromorphic hardware on flexible substrates. However, existing synthesis methods for MoS2, a material capable of superior and stable neuromorphic operation, involve high-temperature processes, posing significant limitations on direct growth onto flexible substrates.

In this study, MoS2 was directly synthesized onto flexible substrates via low-temperature plasma to fabricate a synaptic array and perform vector multiplication, which forms the basis of AI computations. The successful execution of vector multiplication was enabled by the rich grain boundaries of the synthesized MoS2, providing a stable resistive switching filament path, and demonstrated the maintenance of such hardware functionality even under bending.

EM-TuP-6 Efficient Scaling of Ruthenium Thin Films by ALD for High-Volume Manufacturing, *Parmish Kaur*, B. Eychenne, M. Kääriä, A. Sood, Picosun Oy, Finland

Ruthenium (Ru) is highly regarded for its remarkable electrical conductivity, chemical stability, and catalytic activity, rendering it indispensable in electronic, energy, and catalysis applications. Nonetheless, the prohibitive cost associated with Ru precursor materials impedes its widespread utilization.

This study investigates the deposition of Ru films via Atomic Layer Deposition (ALD) to explore its potential for high-volume manufacturing. Employing batch processing of substrates enhances operational efficiency and cost-effectiveness. The Ru films demonstrate a growth per cycle (GPC) of 0.35 Å cy^{-1} at 250 °C, with a density of 12.3 g/cm^3 and surface roughness below 0.7 nm. Electrical resistivity of all films falls below 15 μΩ cm, indicative of highly conductive films.

Grazing incidence X-ray diffraction (GI-XRD) analysis affirms the crystalline structure of the films as hexagonal P63/mmc metallic Ru, while scanning electron microscopy (SEM) underscores their excellent conformal coverage. Minimal impurity content, as evaluated through time-of-flight elastic recoil detection analysis (TOF-ERDA), is observed.

Scaling up the Ru deposition process yields a notable 14-fold enhancement in precursor efficiency, yielding films endowed with desirable physical properties. Thus, the exploration of Ru ALD not only tackles economic challenges but also paves the way for the integration of Ru-based materials into cutting-edge technologies, fostering innovation and progress across diverse domains.

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EM-TuP-7 Luminescent Lanthanide-Organic Hybrid Materials by Atomic/Molecular Layer Deposition, *Melania Rogowska*, P. Hansen, O. Nilsen, University of Oslo, Norway

Trivalent lanthanide ions (Ln^{3+}) show attractive optical properties like luminescence emission from ultraviolet (UV) to visible and even near-infrared (NIR) range depending on the metal ion used. In addition, they can participate in a unique photon upconversion process that requires interaction between two or even more Ln^{3+} ions. Such Ln^{3+}-doped materials could be implemented in various applications including solar cells, lasers, sensors, and bioimaging. The Ln^{3+} ions suffer, however, from weak light absorption and therefore inefficient direct excitation. Moreover, pure lanthanide oxides often display a concentration quenching, and in a consequence a lack of luminescence. These problems can be overcome by coupling species like organic ligands that can participate in energy transfer processes. In this sensitized luminescence, light is absorbed by the organic ligand, and energy is transferred to Ln^{3+} ions where the luminescence is generated. Furthermore, the presence of organic ligands can provide the separation between Ln^{3+}ions to overcome the concentration quenching.

Molecular layer deposition (MLD) is a suitable tool to produce such luminescent organic-inorganic hybrid Ln^{3+}-based materials with ultrahigh precision. This technique allows for accurate composition, thickness, and conformality control on a nanometer scale, which is specifically important for potential applications of luminescent materials as thin films and coatings. In this work, hybrid thin films were deposited using the β-diketonate Ln(thd)$_3$ precursors as a Ln^{3+} source (such as Nd^{3+}, Eu^{3+}, Tb^{3+}, and Yb^{3+}), and various aromatic dicarboxylic acids as organic linkers (including 1,4-benzenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid). In addition, lanthanide fluorides (LnF$_3$) were incorporated into the films forming multilayer nanocomposite structures with more than one Ln^{3+} component showing strong luminescence emission. The final goal of this work is to create multilayer upconverting luminescent Ln^{3+}-based materials.

EM-TuP-10 Structural and Electrical Properties of Ta-Doped TiO$_2$ Prepared by Supercycle Atomic Layer Deposition, *Iqtidar Wasif*, FHR Anlagenbau GmbH, Semiconductor Physics, Chemnitz University of Technology, Germany; *H. Bryja, A. Muhammad, S. Simon*, FHR Anlagenbau GmbH, Germany; *N. Balayeva*, Semiconductor Physics, Chemnitz University of Technology, Germany; *J. Barzola Quiquia, M. Reinfried*, FHR Anlagenbau GmbH, Germany; *D. Zahn*, Semiconductor Physics, Chemnitz University of Technology, Center for Materials, Architectures, and Integration of Nanomembranes (MAIN), Chemnitz University of Technology, Germany

TiO$_2$ has been intensively studied as a transparent conductive oxide and photoanode for photovoltaic and photocatalytic applications. The conductivity of TiO$_2$ can be improved by doping with group V elements such as Nb or Ta. However, effectively tailoring their properties by means of controlled doping amounts is challenging. Atomic layer deposition (ALD) offers an accurate tuning of the elemental composition by alternating binary ALD processes in a supercycle approach. This work aims at the

supercycle deposition of Ta-doped TiO_2 by thermal ALD and the effect of doping and annealing conditions on the structural and electrical properties of Ta: TiO_2 thin films. Titanium (IV) isopropoxide (TTIP) and (tert.-Butylimido)-tris-(ethylmethylamido)-tantalum(V) (TBTEMTa) are used as titanium- and tantalum-precursors, respectively, and water as a co-reactant.For the characterization of the structural properties of the thin films, Raman spectroscopy and X-ray diffraction (XRD) are used. The elemental compositions of the films are characterized by X-ray photoelectron spectroscopy (XPS) and/or energy-dispersive X-ray spectroscopy (EDX). Finally, the electrical properties are investigated to study the effects of different doping concentrations. The results show that by using the supercycle atomic layer deposition we have successfully modified the electrical properties of TiO_2 by systematic doping with Ta, which makes it attractive for future applications.

EM-TuP-11 Molecular Layer Deposition of Ferrocene-Based Thin Films, *Justin Lomax,* University of Western Ontario, Canada*; E. Goodwin,* Carleton University, Canada*; J. Bentley, J. Bosso,* University of Western Ontario, Canada*; C. Crudden,* Queen's University, Canada*; S. Barry,* Carleton University, Canada*; P. Ragogna,* University of Western Ontario, Canada

Ferrocene is known for its stable and reversible redox properties which makes it a promising candidate for crafting precisely controlled redox-active layers *via* atomic layer deposition (ALD).[1,2] Current microelectronic manufacturing faces challenges with the inability to further scale to smaller features due to defects and edge placement errors with modern deposition techniques. This study explores the application of ferrocene-based precursors in selective vapor and solution deposition processes, aimed to develop redox-active organic layers to act as molecular binary switches for storing memory. Our approach uses ferrocene-appended molecules to achieve well-defined, high-quality layers on targeted metal substrates (Au or Cu) while avoiding non-growth regions. Small molecule synthesis, evaluation of precursor suitability, and characterization of films using Thermogravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and Atomic Force Microscopy (AFM) techniques will be discussed.

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EM-TuP-13 Atomic-Layer Deposition Techniques to the Deposition and Post-Synthesis Modification of Metal-Organic Frameworks, *Catherine Marichy, B. Gikonyo, S. De, A. Fateeva, C. Journet,* laboratoire des multimatériaux et interfaces (LMI), France

Metal-organic frameworks (MOFs) are a class of crystalline materials composed of metal ions/clusters as nodes bridged by organic moieties. These materials often exhibit remarkably high accessible specific surface areas, uniform and tunable pore volumes, and chemical modularity.MOFs have been synthesized mainly as powder or single crystals. However, to integrate these hybrid materials into microelectronic, thin films are needed. Different solution-based approaches, like layer-by-layer deposition,[1] have been developed to grow MOF films but solvent contamination limits their applications like in electronics domains.[2] Atomic/molecular layer deposition (ALD/MLD) approaches therefore circumvent this challenge as solvent-free MOF films with good quality, uniformity, and conformality are grown. In our group, we use ALD techniques to (a) directly deposit MOF thin films on solid substrates and (b) modify bulk MOFs by post-synthesis modification to adjust their properties, providing new functionalities while preserving the network structure.

(a) First direct growth of Copper-based MOFs by ALD/MLD is presented. Paddle-wheel frameworks, as copper terephthalate (Cu-TPA) and MOFs based on electrochemical active ligands as porphyrines, are successfully deposited using a home-made reactor. The obtained films are characterized using ellipsometry, UV-Visible, and IR spectroscopies, powder X-ray diffraction and scanning electron microscopy.

(b) To modify MOFs, in particular to incorporate metal cation in their reactive sites, vapor-phase infiltration (VPI) is also employed.[5] Herein, post-synthesis modification of microporous porphyrin-based MOFs by VPI will be introduced Using pulses of a single precursor (diethylzinc or trimethylaluminium), isolated metallic entities are installed in the stable and microporous Zr(IV)-based porphyrinic MIL-173(Zr) bulk MOF. Indeed, two reactive sites are present: the porphyrin core (free base), and a phenolic group in the meta position of the linker. The structural characterizations and spectroscopic properties of the modified MOF are presented.

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EM-TuP-14 A New Step Towards Crystalline III/V Semiconductors by ALD, *Thilo Hepp,* Philipps Universität Marburg / Dockweiler Chemicals GmbH, Germany*; P. Ludewig,* Philipps-Universität Marburg / Dockweiler Chemicals GmbH, Germany*; O. Briel, J. Koch,* Dockweiler Chemicals GmbH, Germany*; K. Volz,* Philipps-Universität Marburg, Germany

The production of III/V semiconductors by Atomic Layer Deposition (ALD) faces significant obstacles that hinder their widespread application. The selection of suitable precursor materials proves challenging because they must react with III/V semiconductor surfaces in a self-limiting manner to meet the requirements of the ALD process [1]. Good results have been published using alkyl-silyl based precursors [2]. However, a crystalline structure has not been achieved, impacting the efficiency and reliability of the semiconductors. Crystalline semiconductors are important for electronic and optical applications.

In addition, the inadequate leak tightness of conventional ALD systems leads to high oxygen incorporation in the epitaxial layers, resulting in detrimental defects. Oxygen is a deep trap in the band gap of semiconductors that significantly reduce the lifetime of optical devices.

To overcome these obstacles, the Philipps-University Marburg and Dockweiler Chemicals collaborate jointly. The Philipps-University will use its extensive expertise in CVD processes to optimize processes and develop innovative techniques. For this purpose, a MOCVD system has been rebuilt by the Sempa Systems GmbH to enable processes in a leak-tight tool as required for deposition of high quality III/V semiconductors.

Dockweiler Chemicals will focus on developing tailored chemicals to enhance the properties of the deposited material, such as crystallinity. Through this collaboration between academic research and industrial innovation, we aim to jointly address the challenges of ALD-based III/V semiconductor manufacturing and open new perspectives for the semiconductor industry.

A promising material system to dive into ALD of III/V semiconductors is GaP, which is, for example, an ideal buffer layer for the deposition of compound semiconductors on silicon (Si) for various applications such as lasers on Si or tandem absorbers [3]. In particular, the nucleation of GaP on Si 300 mm (001) wafers requires a delicate process and is challenging to control using MOCVD. A self-limiting ALD process would inherently produce a uniform layer on arbitrarily large substrates. However, crystal quality of III/V semiconductors gown by ALD remain a challenge. First results using alkyl-silyl precursors will be compared with samples grown using standard MOCVD precursors in a close coupled shower head reactor.

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EM-TuP-15 Pushing the Boundaries: Advancing Resist Technology for Beyond EUV Lithography Application, *Dan Le, T. Chu,* University of Texas at Dallas*; W. Lee,* stony Brook University*; N. Tiwale,* Brookhaven National Laboratory*; J. Veyan, J. Kim, D. Kim, M. Lee,* University of Texas at Dallas*; C. Nam,* Stony Brook University/Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas

Besides extending EUV lithography (EUVL) technology by utilizing optic systems with numerical apertures exceeding 0.55 (higher-NA EUVL) or even surpassing 0.75 (hyper-NA EUVL), reducing lithography wavelength (λ) from 13.5 to 6.7 nm has been of interest to accommodate the extreme downscaling of device critical dimension [1]. Alongside advancements in light sources and optical systems, the adoption of novel resist platforms is an important key factor for the readiness of 6.7 nm-based technology due to a reduction in material sensitivity [2].

Herein, we investigate the potential of a Zn-based hybrid thin-film system that is synthesized via ALD analog as a part of the *dry* resist platform for beyond EUV (BEUV) lithography technology. The growth characteristics and material stability of Zn-based hybrid thin films are evaluated, with the

highest growth rate observed at 75°C (Figure 1a). Upon being exposed to electrons with energy similar to those of photons at 6.7 nm wavelength (~180 eV), the Zn-based inorganic-organic hybrid thin films exhibited negative tone characteristics when developed using diluted KOH solution (Figure 1b). The low-energy electron beam lithography (EBL) will be employed to rapidly assess the material sensitivity, with height profiles obtained using an atomic force microscope (AFM). Furthermore, we extend our focus on understanding the chemical alternations of the Zn-based hybrid thin films when exposed to electrons with energy similar to or lower than those of BUEV photons. The experiment is conducted using our unique *in-situ* FTIR system equipped with an electron flood gun and a residual gas analyzer (RGA). The *in-operando* RGA spectrum (Figure 2) indicates H_2, H_2O, CO, and CO_2 as byproducts produced during the electron exposures. The crosslinked mechanisms of Zn-based inorganic organic hybrid thin films are elucidated through *in-situ* IR absorbance and *in-operando* RGA analysis. A comparison between Zn-based and Al-based hybrid thin film patterning characteristics will also be conducted. This study highlights the potential of novel metal-containing hybrid thin films as a part of the *dry* resist platform and offers valuable insight for the development of novel resist technology for beyond EUVL applications, thus contributing to the ongoing advancement of lithographic techniques.

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EM-TuP-16 Multistep Inorganic Synthesis of Redox-Active THz Phononic Structure, *Norifusa Satoh,* National Institute for Materials Science, Japan; *R. Gordon,* Harvard University

The logic of chemical synthesis (Nobel prize in Chemistry 1990) originally for organic molecules is nowadays observed in inorganic synthesis, especially for the latest electronic device, known as atomic layer deposition (ALD), selective-area deposition, and atomic layer etching. To extend the synthetic strategy toward synthesis of atomically precise dot supper-lattices which cannot be obtained by other methods like molecule beam epitaxy (Nobel prize in Physics 2000), we herein propose an oxide-based combination of ALD and atomically precise dot deposition [ref. 1-3], because we can expect the following four advantages: (1) the strong ionic covalent bonds of oxides keep high melting points even on nanoscale dots to maintain the atomically precise structure without protective ligands [ref. 2,4]; (2) ALD precursors easily chemi-adsorb on the bare surface of oxide dots; (3) the separated oxide dots due to the original organic spacers are conformally solvated by dielectric ALD oxides to show redox reactions as if in solution [ref. 5]; (4) the periods of phononic contrast between the oxide dots and amorphous ALD oxides matches the wavelength of THz phonon over room temperature, less than 1 nm, to confine heat conduction [ref. 6]. In this research, we first confirmed the linear thickness growth based on the number of super cycle, second demonstrated the redox response of oxide dot inside a flash memory structure [ref. 7], and finally evaluated the effect of ALD cycle on thermal conduction using the previous method [ref. 8]. These results suggest the multistep inorganic synthesis may be able to design a new type of electron-phonon interaction or coupling.

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EM-TuP-17 Modelling the Growth of Zincone ALD/MLD Hybrid Thin Films: A DFT Study, *Mario Mäkinen, K. Laasonen,* Aalto University, Finland

Purely inorganic, or organic thin films can be fabricated using either atomic or molecular layer deposition (ALD and MLD). By combining these two methods, one can fabricate hybrid thin films, which contain both organic and inorganic layers, and thus will drastically improve the applicability of the thin film technology. Even though this deposition method has been used extensively experimentally, the reaction paths occurring during the thin film deposition process are still widely unknown. Density functional theory (DFT) -based modeling answers this problem, as we can study the growth mechanisms of hybrid thin films on an atomic-level accuracy.

Hybrid thin films under investigation were studied using gas-phase and surface reaction models, of which examples are presented in Figure 1. The surface models consisted of two differently ethyl-saturated zinc oxide surfaces, which account for the imperfection of the thin film growth, and the adsorbing organic precursor 4-Aminophenol. The gas-phase models consisted of diethyl zinc and an organic molecule from a variety of aliphatic and aromatic compounds.

Modelling of the reaction pathways was conducted using the GPAW program. DFT was used with the PBE exchange and correlation functional. Van der Waals correction TS09 was used due to weak interactions caused by the ethyl ligands. All the reaction barriers were calculated using the nudged elastic band -method with a climbing image (CI-NEB).

4-Aminophenol reacts faster and more strongly with its hydroxyl than its amino group, which will dictate the alignment of 4-Aminophenol in the film structure. 4-Aminophenol adsorbed to the surface through physisorption, and after that, the hydrogen will migrate to ethyl ligand within a complicated branching reaction chain. This process, of which an example is illustrated in Figure 2, utilizes primarily a ligand exchange but also a dissociation reaction. The amount of ethyl ligands partaking in the growth reaction of the hybrid thin film was approximately 20 to 25 percent. Different macrostructures of these hybrid thin films were compared and the effect of oxygen on the growth reaction mechanisms was discovered.

Gas-phase models were utilized in the screening of over a dozen compounds to discover the relative reactivity of different functional groups present in aliphatic and aromatic organic precursors. Our results on both the reactivity and bond strength between different functional groups agree qualitatively with experimental results. Thus, this rapid screening process enables the feasibility prediction of the potential organic precursors, and it can be expanded to hundreds of precursors.

EM-TuP-19 Tuning the Diffusivity of DEZ During Vapor Phase Infiltration in Photopatternable Polyacrylates by Increasing the Polymer Network's Flexibility, *Lisanne Demelius, A. Coclite,* Graz University of Technology, Austria; *M. Losego,* Georgia Institute of Technology

The kinetics of vapor phase infiltration (VPI) can be very complex due to various operational factors and intrinsic properties affecting precursor sorption and diffusion. These factors include the precursor's vapor pressure, process temperature, precursor size, the density of reactive polymer groups, precursor-polymer reaction rates, and polymer free volume. Understanding the transport and reaction mechanisms is crucial for the successful optimization of VPI processes and their application to new precursor-polymer systems.

In this work, we investigate diethyl zinc (DEZ) infiltration into highly crosslinked polyacrylates, a class of materials that has not been previously studied for VPI. Our findings reveal that in such a densely crosslinked system, diffusion becomes the limiting factor. By copolymerizing trimethylolpropane triacrylate (TMPTA) with its ethoxylated counterpart (ETPTA), which has longer and more flexible side chains, we could significantly enhance DEZ diffusion, highlighting the role of polymer free volume in VPI kinetics. X-ray photoelrctron spectroscopy (XPS) depth profiles showed that while only partial Zn infiltration is achieved for a 200 nm homopolymer film of pTMPTA even after 50 h of DEZ exposure, adding 10 wt.% of ETPTA is enough to allow for full infiltration of the polymer layer. At 25 wt.% of ETPTA, the time required to achieve complete infiltration with DEZ is reduced to 15 h, and at 75 wt.% it is as short as 2 h. In a similar manner, reducing the UV polymerization time of the photopolymers and thus decreasing their crosslinking density also improves DEZ diffusion. The observed transport behavior is in good agreement with the theoretical reaction-diffusion model for VPI developed by Ren, McGuinness et al.[1].

The polyacrylate system studied in this work is of particular interest for VPI because its photopatternability opens new avenues for the creation of hybrid organic-inorganic nano- and microstructures by integrating VPI with existing polymer patterning techniques. As a proof of concept, we demonstrate the selective DEZ infiltration of a photolithographically patterned p(TMPTA-c-ETPTA) copolymer film on poly (methyl methacrylate) (pMMA). Energy-dispersive X-ray spectroscopy (EDX) elemental mapping and XPS depth profiles confirmed that Zn was present only in the patterned copolymer structures, but not in the poorly infiltrating pMMA.

Overall, our findings advance the understanding of VPI process kinetics, and lay an important foundation for applying VPI to highly crosslinked

polyacrylates for top-down property modification of photopatternable polymer structures.

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EM-TuP-20 Tailoring Pore Size and Surface Hydrophilicity in Ceramic Membranes: The Case of MLD-Grown Titanicone Layers, *Harpreet Sondhi, A. Nijmeijer,* Inorganic Membranes, University of Twente, Netherlands*; A. Kovalgin,* Integrated Devices and Systems, University of Twente, Netherlands*; F. Roozeboom,* University of Twente and Carbyon B.V., Netherlands*; M. Luiten-Olieman,* Inorganic Membranes, University of Twente, Netherlands

Membranes are used at large scale to purify surface or wastewater and are increasingly applied in nanofiltration (pore size range 1-10 nm) of organic solvents. However, mass organic solvent streams containing small molecules are still treated with traditional energy-intensive technologies like distillation. Here, polymeric membranes suffer from swelling, which can change pore sizes significantly due to solvent-membrane interaction. In contrast, ceramic membranes are hydrophilic and thus more robust yet challenging to reproduce commercially. In this study we have used Molecular Layer Deposition (MLD) to modify high-porosity Al_2O_3-based ceramic membranes with average pore size of 20 nm, by coating their internal surface with hybrid layers grown by MLD. Objectives were to 1) narrow the membranes' pore size and pore size distribution by depositing a TiO_2 layer (acting as an intermediate) from $TiCl_4$ and EG (ethane-1,2-diol). 2) To investigate the hydrophilicity of hybrid layers grown by MLD from $TiCl_4$ and three different organic co-reactants, being heptanol, 3-aminopropyltriethoxysilane (APTES), and n-phenyltrimethoxy-silane (n-PTMS). Depositions were carried out at temperatures ranging from 100 to 200 °C, pulse times ranging from 0.1 to 0.4 sec for $TiCl_4$, 1 to 20 sec for the co-reactants, and 60 to 120 sec for N_2 purging. Typically, using MLD, the average pore size of the bare ceramic support (≈20 nm) could be reduced below 2 nm, as determined by permporometry, for 10 nm TiO_2 layer, see Fig. 1. The three hybrid layer types were also grown with identical process recipes on planar silicon substrates. This way, they could be tested on their surface hydrophilicity and chemical stability in different solvents (see Fig. 2),

- Surface hydrophilicity was measured by way of measuring the respective Water Contact Angle (WCA). These WCA values were 109° (heptanol), 106° (APTES), and 114° (n-PTMS).
- Chemical stability was measured by immersing the samples in solvents with decreasing polarity: water > acetone > ethyl acetate > hexane. The n-PTMS-based hybrid layer showed the most promising results:exhibiting excellent stability against hexane (non-polar), without layer degradation or change in its wetting performance (WCA constant at 114° after 24 hrs and seven days). While the heptanol- and APTES-based layers reacting with solvents lost hydrophobicity (WCA reducing to < 90°).

The results obtained so far provide new insights into the effect of using different organic co-reactants in MLD to optimize pore size and surface hydrophilicity to improve ceramic membranes' performance in organic solvent nanofiltration.

EM-TuP-21 Flexible Conductive Hybrid: Indium Oxide-ParyleneC Obtained by Optimized Vapor Phase Infiltration, *Oksana Yurkevich,* CIC NanoGUNE, Spain*; E. Modin,* CIC nanoGUNE, Spain*; I. Šarić Janković, R. Peter, M. Petravić,* Department of Physics and Centre for Micro- and Nanosciences and Technologies University of Rijeka, Croatia*; M. Knez,* CIC nanoGUNE, IKERBASQUE Basque Foundation for Science, Department of Physics and Centre for Micro- and Nanosciences and Technologies University of Rijeka, Spain

The advancement in enhancing traditional organic or inorganic materials has reached a plateau, necessitating a significant step forward by concurrently exploiting the properties of both organic and inorganic materials. Over the last decade, vapor phase infiltration (VPI) has gained substantial attention as a versatile top-down approach for crafting hybrid materials. Various hybrid systems, incorporating a blend of metal oxide and polymer, have been developed. Of particular interest is In_2O_3, an essential component in materials employed for transparent electrodes such as indium tin oxide or indium zinc oxide, pivotal for the electronics industry.

Our research focuses on the creation of a hybrid material based on indium oxide and Parylene C and further polymers of technological relevance. The polymer in our approach serves as a dielectric and flexible polymeric matrix. To gain a deeper understanding of this hybrid material system, we examine the impact of the oxygen source on VPI of indium oxide into Parylene C using trimethylindium (TMIn) and three distinct oxygen-containing precursors, water (H_2O), hydrogen peroxide (H_2O_2) and ozone (O_3). Through the application of these processes to the polymer, we analyze the hybrid Parylene C/In_xO_y samples by transmission electron microscopy (TEM), depth-profiling with secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectrometry (XPS). The study contrasts the differences between the various precursor combinations.

Our findings reveal that employing hydrogen peroxide as the second precursor in a TMIn-based VPI process is advantageous compared to using water. The reactivity of H_2O_2 contributes to higher growth rates, deeper infiltration, and lower onset temperatures for crystallite formation of indium oxide in the $TMIn/H_2O_2$ process compared to $TMIn/H_2O$, while ozone degraded the polymer chains and a lowered its mechanical flexibility, limiting the applicability of $TMIn/O_3$ process. The resulting hybrids are conductive and exhibit sheet resistance values as low as 3 k$\Omega/\square$ without additional annealing. Furthermore, these hybrids display a surprising ability to heal ruptures and defects in the conductive layers on their surface. Given that Parylene C is a dielectric and indium oxide is a wide band gap semiconductor, the amalgamated flexible conductive hybrids hold great promise for applications in electronics, such as flexible electrodes in wearables, displays, solar cells, or medical sensors.

EM-TuP-22 ALD Ternary Films and Nanolaminates Based on Al_2O_3, Zro_2 and Zno, *Piotr Polak, J. Jankowska-Śliwińska, L. Stańco, J. Maleszyk, A. Łaszcz,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland*; A. Wolska, M. Klepka, K. Jabłońska,* Institute of Physics, Polish Academy of Sciences, Poland*; H. Stadler,* Bruker Nano Surfaces, Germany*; K. Kosiel,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

Metal oxide nanocoatings show strong application potential in many areas including anti-corrosion protection, surface engineering of polymers, medical materials, or electrode/electrolyte interfaces in all-solid-state batteries, to name just a few. Precise tuning of the functional properties of coatings, however, creates the need to fabricate materials that are more complex than binary ones. ALD is an excellent tool for fabrication such conformal multi-component thin-film coatings, enabling strict control of their thickness and composition or doping profiles. However, the ALD of such complex layers is usually far from satisfying the rule of mixtures and does not provide a linear dependence for growth-per-cycle and composition on the relevant parameters specific to the growth of binary materials. Therefore, surface engineering using multi-component ALD oxides requires in-depth experimental knowledge on layer growth using various substrates.

For our research we used ALD Beneq TFS-200 equipment. We experimentally tested thermal ALD of Al_2O_3, ZrO_2 and ZnO thin films, as well as their mixtures (three different ternaries) and nanolaminates. For deposition of complex films we used a supercycle approach. The processes temperature range was 100-300°C. The films were generally only several tens of nanometers thick, and most were less than 20 nm. Silicon and gallium arsenide were used as substrates. We used trimethylaluminium, tetrakis(ethylmethylamino)zirconium (IV) and diethylzinc as chemical precursors for Al, Zr and Zn, respectively. We alternatively used deionized water or ozone as oxygen precursors. We proved the possibility of controlling the thickness and composition, though they typically deviated from the properties expected by the rule of mixtures. Thickness and composition of the films were analysed by a combination of spectroscopic ellipsometry, transmission electron microscopy energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. For selected films we analysed also coating tightness, surface topography and electrical properties using atomic force microscopy (by tapping mode and conductive AFM).

EM-TuP-24 Thin Film Composite Desalination Membranes by Molecular Layer Deposition, *Brian Welch, R. Cai,* Technion Israel Institute of Technology, Israel*; V. Rozyyev, J. Elam,* Argonne National Laboratory, USA*; T. Segal-Peretz,* Technion Israel Institute of Technology, Israel

The conventional preparation of thin film composite (TFC) reverse osmosis membranes involves interfacial polymerization (IP) atop a porous,

polymeric support. This process can create selective polyamide films 100+ nm thick, with complex, yet relatively inhomogeneous morphologies. While commercially successful, IP is limited in its ability to control the selective layer composition, thickness and morphology which hinders transport properties and operational lifetime.

To overcome the limitations, we have developed TFC reverse osmosis membranes using all-organic molecular layer deposition (MLD) rather than IP. Key to fabrication was the ability to grow the MLD film across the pore openings of a porous substrate despite the conformal nature of MLD. To do so, we developed a sacrificial polyvinyl alcohol (PVA) pore filling process that enabled growth atop porous polyethersulfone supports while avoiding undesirable infiltration effects. Selective polyamide MLD films were made from m-phenylenediamine and trimesoyl chloride precursors at 3 Å/cy, 120°C. Vapor phase infiltration of the organic precursors into the PVA was investigated with in-situ ellipsometry. In crossflow desalination tests, MLD TFC membranes had improved water flux and NaCl rejection compared to commercial IP membranes. Improvements in performance were attributed to differences in the synthesized materials: compared to IP, MLD films were dense, highly crosslinked, and morphologically conformal, without nanoscale voids. Furthermore, a tradeoff between flux and salt rejection could be tuned by varying the thickness and composition of the MLD selective layer. This research has broad implications for this and other applications which use TFCs, such as gas separations and nanofiltration.

EM-TuP-25 Complex Materials for Next Generation Electronics and Photonics - ALD will Prevail!, *Henrik H. Sønsteby*, University of Oslo, Norway

Even though semiconductor industry is doing a great job in tearing down scaling walls to increase the longevity of traditional Si-technology, new materials solutions are inevitably needed to harness the greatness promised by future ICT. This includes true edge computing for the ultra-connected smart society, as well as novel devices for neuromorphic computing. It is only natural that different technologies and device architectures are developed for different use - and with this more dedicated materials solutions for different applications.

These new materials will still need to adhere to many of the same processing constraints that we know from Si-ICT, such as low thermal budget, extreme conformality and thickness control - making ALD the most (if not the only) viable synthesis technique also as we look towards the next generations.

In this work we present how we are purposefully crafting an ALD catalogue of complex oxides with a wide range of functional properties. This includes materials that exhibit ferromagnetic, ferroelectric, metallic and semiconducting behavior, as well as combinations of these functionalities. We show how the quirks of ALD-processes and precursors can be exploited to enable low-temperature epitaxy of these materials. We point at cation substitution with high compositional control, strain engineering by careful choice of substrate and strategic process design to enable high quality crystal growth.

Materials such as $RENiO_3$ (RE = La - Lu), $BaTiO_3$, $NiFe_2O_4$ and $BaSnO_3$ are used as examples of materials with different functionalities, and where distinct ALD process design is needed to facilitate crystal growth. We introduce some ideas that aid ALD process design for complex oxides - letting us quickly tune in to optimal conditions.

We strongly advocate for the pivotal role of ALD in advancing ICT through the utilization of dedicated materials for emerging technology paradigms. However, this expansion imposes new challenges on ALD process development, necessitating innovative solutions. Through this work, we address these challenges and propose strategies to overcome them.

EM-TuP-26 Nanomolecularly-Induced Effects on the Synthesis and Stability of Multilayered Titania/Organophosphonate Interfaces, *C. Rowe,* Rensselaer Polytechnic Institute*; A. Kashyap,* Indian Institute of Technology, Mandi, India*; G. Sharma,* Rensselaer Polytechnic Institute*; N. Goyal,* Indian Institute of Science, Bangalore, India*; J. Alauzun,* University of Montpellier, France*; S. Barry,* Carleton University, Canada*; N. Ravishankar,* Indian Institute of Science, Bangalore, India*; A. Soni,* Indian Institute of Technology, Mandi, India*; P. Eklund, H. Pedersen,* Linköping University, Sweden*; Ganpati Ramanath,* Rensselaer Polytechnic Institute

Nanoscale hybrid inorganic-organic multilayers are attractive for accessing emergent phenomena and properties through superposition of nanomolecularly-induced interface effects. Here, we demonstrate the effects of interfacial molecular nanolayers (MNLs) of organo-diphosphonates on the growth and stability of titania nanolayers during the synthesis of titania/MNL multilayers by sequential atomic layer deposition and single molecular layer deposition pulses. Electron microscopy, X-ray reflectometry and Rutherford backscattering spectrometry reveal that interfacial organo-diphosphonate MNLs result in ~20-40% slower growth of amorphous titania nanolayers than those grown at identical conditions without MNLs. The MNLs also inhibit anatase nanocrystal formation from the amorphous titania nanolayers. Both effects are more pronounced in multilayers with aliphatic-backbone-MNLs than those with aromatic-backbone-MNLs. Elastic recoil spectroscopy analyses reveal a MNL-induced increase in impurity incorporation from the titanium precursor. These results collectively suggest MNL-induced diminution of growth kinetics and suppression of nanocrystal formation are likely due to incomplete and/or altered surface reactions. Both aliphatic- and aromatic-backbone MNLs result in twofold higher film roughness, suggesting that roughening is primarily due to MNL bonding chemistry. Such MNL-induced effects on inorganic nanolayer growth rate, roughening and stability are germane to realizing high-interface-fraction hybrid organic-inorganic nanolaminate multilayers.

EM-TuP-27 Comparative Analysis of Film Growth in Molecular Layer Deposition: Siloxane-Bridged Silane Precursor vs. Methylene-Bridged Silane Precursor, *Man Hou Vong, M. Dickey, G. Parsons,* North Carolina State University

Molecular layer deposition (MLD) of siloxane-based polymers can be highly useful because these polymers (for example, polydimethylsiloxane) have vast applications in different fields. However, previous literature reported that MLD of siloxane-based polymer using homo-bifunctional siloxane-bridged silane molecules was ineffective due to the lack of film growth.[1] In this work, the growth of siloxane-based polymers in MLD using siloxane-bridged (Si-O-Si) silane precursor and water was investigated and compared to the growth of carbosilane-siloxane film using methylene-bridged (Si-CH_2-Si) silane precursor and water. Our results show that the film deposited with methylene-bridge precursor can grow beyond 1 nm whereas the film deposited with siloxane-bridged ultimately stops growing after the film thickness reaches only a few angstroms. This finding suggests that the rigidity of the bond angle between the functional groups may play a role in mitigating the occurrence of "double reaction" – that is, the functional groups on both ends of the precursor react with the surface of the substrate – which results in promoting film growth. The findings reported in this work also provide insights into the growth mechanism of ultra-thin organic thin films.

1: Pinna, N; Knez, M.; *Atomic Layer Deposition of Nanostructured Materials*; Wiley-VCH, 2011, p. 99-102

EM-TuP-30 Physical, Chemical and Architectural Metal-Ceramic Nanolaminate Design for Enhanced Mechanical Properties, *A. Sharma,* Swiss Cluster AG, Switzerland*; S. Tsianikas, J. Michler, X. Maeder,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; Carlos Guerra-Nuñez,* Swiss Cluster, AG, Switzerland

Metal multilayer composites can show an enhancement of both strength and ductility related to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [1-2]. However, nanolaminate structures often suffer microstructural instability during annealing and extreme deformation conditions. It is well known that the alloying addition in bulk nanocrystalline materials can significantly improve the microstructural stability and mechanical properties by grain boundary pinning, secondary phase precipitation and other segregation related mechanisms. Although there is ample literature available on the mechanical behaviour of pure metallic nanolaminate structures, the experimental results of the effect of alloying addition on the microstructural stability and mechanical properties in the metal nanolaminated structures is rather limited.

Here, we present recent experimental data on the fabrication and mechanical behavior of nanolaminate FCC-BCC high entropy alloy thin films with interlayer thickness 50 nm and Cu-Al thin films with interlayer thickness 30, 50 and 120 nm.The layers are separated by atomic layer deposition of 2 nm amorphous Al_2O_3 layer without breaking the vacuum in a new Cluster System combining both ALD and PVD in the same equipment (Swiss Cluster AG). As a model system, FCC-NiCoCrFe and BCC- NiCoCrFe-Al (with Al ~20 at. %) and Cu_{1-x} – Al_x (X: 0, 5 and 10 at.%) layers with a total thickness of 3 microns is deposited on Si (100) substrate by magnetron sputtering and subsequently tested by micro compression experiments. The mechanical response of the multi-layered structures is also compared with single-layer counterparts. It is observed that presence of ALD layers significantly improves the strength and ductility in the films. Moreover, the

multilayered microstructure takes advantage of multiple small-scale mechanisms such as Hall-Petch, solid solution, and Orowan precipitate strengthening for enhanced mechanical properties compared to bulk. The post-mortem electron microscopy investigation provides insight into deformation mechanisms in the individual layers.

1. S.J. Zheng, I.J. Beyerlein, J. Wang, J.S. Carpenter, W.Z. Han, N.A. Mara, Acta Materialia, 60 (2012) 5858-5866.

2. N. Mara, I. Beyerlein, J Mater Sci, 49 (2014) 6497-6516.

Wednesday Morning, August 7, 2024

ALD Applications
Room Hall 3D - Session AA1-WeM

Flash and Ferroelectric Memories

Moderators: **Haripin Chandra**, EMD Electronics, USA, **Matti Putkonen**, University of Helsinki

8:00am **AA1-WeM-1 Ferroelectric Doped HfO₂: From Ald Processing to Device Applications**, *Uwe Schroeder,* Namlab, Germany **INVITED**
Extensive research and development have been conducted on doped HfO_2 or ZrO_2-based ferroelectric materials [1]. These unique fluorite-structured ferroelectrics have outstanding potential for commercial applications due to their scalability, CMOS compatibility, and ease of fabrication. Ferroelectric HfO_2 is particularly attractive for semiconductor memory applications because of its advantageous properties. The scientific community has made great efforts to improve and optimize the ferroelectric properties using a variety of approaches due to the wide range of conditions under which ferroelectricity can occur in thin films. Consequently, thin-film ferroelectric capacitor and memory array technologies are advancing quickly. But, researchers are still trying to elucidate the various causes of ferroelectricity in doped HfO_2 and ZrO_2 thin films in order to improve device performance.

Different chemical precursors for HfO_2 and ZrO_2 are compared for the best ALD process window [2]. The doping and oxygen content of the film are important for both the formation of the crystal phase and the performance of HfO_2-based devices [3]. It is crucial to consider all of these factors when designing and optimizing HfO_2-based devices. Other factors, such as interaction with electrode materials, crystallization anneals, and stress in the resulting film, can also significantly affect the ferroelectric properties. Once a ferroelectric phase is reached in thin films, it can be influenced by further thermal treatments and the application of an electric field. Recent piezo-force microscopy studies have confirmed a nanoscale electric field-induced phase transition from a non-polar tetragonal to a polar orthorhombic phase. This knowledge of phase transitions in doped HfO_2- and ZrO_2-based films is essential for the development of future ferroelectric devices.

The recently discovered properties of HfO_2, even at film thicknesses below 10 nm, have enabled a growing number of applications, such as high aspect ratio ferroelectric capacitors (FeCap) and field-effect transistors (FeFET) [4]. Additionally, other applications, such as ferroelectric tunnel junctions, neuromorphic, piezo-, and pyroelectric devices, are being discussed [4]. Many devices can now be realized on smaller technology nodes and in larger memory arrays. At the end of 2023, non-volatile FeCap based memory chips have been presented at conferences [5].

This review will cover recent results and provide an overview of the subject, starting with a discussion of the causes of ferroelectric properties and experimental reports on phase stabilization in doped HfO_2, as well as an introduction to recent semiconductor applications.

8:30am **AA1-WeM-3 Interfacial Layer Engineering by Tungsten Oxide for Ferroelectric La-Doped Hf₀.₅Zr₀.₅O₂ Layer**, *Dae Seon Kwon,* M. Popovici, J. Bizindavyi, imec, Belgium; G. De, A. Delabie, KU Leuven, imec, Belgium; A. Belmonte, G. Sankar Kar, imec, Belgium; J. Van Houdt, KU Leuven, imec, Belgium
In this work, the electrical performance of the ferroelectric La-doped $Hf_{0.5}Zr_{0.5}O_2$ (La:HZO) layer was optimized by interfacial engineering employing tungsten oxide with back-end-of-line (BEOL) compatibility, and the effect was investigated in detail. A major problematic issue arising when scaling down the physical thickness of the HZO for industrial applications is undesirable stabilization of non-ferroelectric tetragonal phase, especially at the interface between the TiN electrode and HZO layers due to a high defect level such as oxygen vacancy. This phenomenon was attributed to the oxygen scavenging effect by the TiN electrode, leading to the formation of oxygen vacancies throughout the HZO layer, and especially at the interfaces. In this study, to stabilize the ferroelectric orthorhombic phase, tungsten oxide was adopted as an oxygen donor for the HZO layer.

Tungsten oxide has numerous advantages, ranging from high compatibility with complementary metal-oxide-semiconductor (CMOS) technology to its various oxidation states, which can control the oxygen vacancy level in the HZO layer when used as an interfacial layer between the TiN electrode and HZO layer. First, the atomic layer deposition (ALD) process of the tungsten trioxide (WO_3) was established, and the characteristics as a potential interfacial layer were examined. Subsequentially, all layers in metal-insulator-metal (MIM) capacitor were deposited via ALD. The oxygen supply from reducible tungsten oxide, transitioning from WO_3 to WO_{3-x}, effectively annihilated oxygen vacancies in the HZO, leading to the promotion of the orthorhombic phase. Additionally, the possible distribution of the oxygen vacancies induced by the interfacial tungsten oxide layer and its effect was investigated depending on the device cycling through the imprint of the polarization-electric field (P-E) loop and the depth profile of the oxygen element. Appropriate control of oxygen vacancies via interfacial engineering with various seed and capping layer materials enabled the stabilization of the orthorhombic phase, thereby increasing the two remanent polarization ($2P_r$) value. Finally, the superior electrical performance of the improved $2P_r$ value with an endurance cycle number over 10^9 cy was achieved with an optimized tri-layer stack consisting of seed TiO_2/La:HZO/capping WO_3. This interfacial engineering work is anticipated to provide a guideline for further engineering involving thickness, dopant, and functional layer in FeRAM capacitor.

8:45am **AA1-WeM-4 Ultrathin HfO₂–ZrO₂ Multilayers Structures by ALD for Embedded Ferroelectric Non-Volatile Memories**, *Amanda Mallmann Tonelli, J. Mercier, N. Vaxelaire, Y. Mazel, Z. Saghi, N. Gauthier, S. Martin, L. Grenouillet, V. Jousseaume, M. Bedjaoui,* CEA-Leti, France
The rapid progress of nanoelectronic systems and miniaturized portable devices has increased the urgent demands for miniaturized and integrated circuit. Recently, the developedhafnium-oxide (HfO_2)basedferroelectric filmswith CMOS-compatible process shows a great potential for advanced low-power device technology [1]. However, ultrathin HfO_2-based ferroelectric films are still in the risk of device failure due to the large leakage current, which makes it unstable and limits the device service life [2], [3]. On the other hand, a significant effort has been made to lower the ferroelectric film thickness below 10 nm while maintaining good ferroelectric properties. The multilayer approach can provides solutions to the problems of leakage current and endurance by blocking the electrons injected from the electrode, which provides a promising idea for the application of HfO_2 in electronic devices [4].

The aim of this study is to develop ultrathin ferroelectric layers by ALD for MFM (Metal-Ferroelectric-Metal) capacitors based non-volatile memories. Within this work, HfO_2-ZrO_2 multilayers consisting of stacked HfO_2 and ZrO_2 were developed and investigated. The objective of this project is i) to investigate the intrinsic characteristics of the material and its evolution at each stage of the MFM fabrication through different structural, physicochemical and image analyses and ii) correlate the structural properties to the electrical characteristics.

The experimental analysis of the 10 nm thick nanolaminates films allowed some preliminary conclusions. The x-ray diffraction results presented in (Fig. 1) reveal that the films are already crystalline after deposition of the TiN/W top electrodes, carried out at 380°C. The diffraction peaks around 30.5° stand for a mixture of tetragonal and orthorhombic phase and could be evidence of the beginning of crystallization of a ferroelectric material. Furthermore, after dry plasma etching of the top electrode, the chemical state of material was analyzed using x-ray photoelectron spectroscopy. In addition to the composition of the material, an estimation of the oxygen vacancies (V_o) was made, as V_o is supposed to play a crucial role in the ferroelectricity of HfO_2-based films (Fig. 2). After annealing, through electrical positive-up-negative-down (PUND) measurement, it was possible to obtain evidence of ferroelectricity of the structure (Fig. 3) The preliminary findings showed in this work seems favorable for the implementation of FE HfO_2-ZrO_2 multilayers in non-volatile memory devices.

9:00am **AA1-WeM-5 Effects of Gamma Radiation on the Electrical and Structural Properties of Ferroelectric Hafnium Oxide-Based Capacitors**, *Samantha Jaszewski, M. Henry,* Sandia National Laboratories
Ferroelectric hafnium oxide (HfO_2) presents opportunities for technological developments in microelectronics, such as scaling of ferroelectric random-access memory (FeRAM) and new devices such as ferroelectric field-effect transistors (FeFETS) and ferroelectric tunnel junctions (FTJs), that were not previously possible with conventional ferroelectrics. This is due to its compatibility with silicon and ability to exhibit a ferroelectric response in films as thin as 1 nm.Understanding the interaction between radiation and HfO_2-based ferroelectrics is necessary before this material can be utilized in devices facing radiation-hostile environments. In this work, the effects of varying doses of gamma radiation (1 to 8 Mrad) on the structural and electrical properties of metal-ferroelectric-metal capacitors fabricated with 17 nm thick hafnium zirconium oxide (HZO) layers is investigated.

Additionally different electrode materials, titanium nitride and tungsten, will be compared. Polarization-electric field, capacitance-voltage, and leakage current measurements were made after electric field cycling with voltages ranging from 2.6 to 4 V. It will be shown that the devices experience decreased endurance and a shift in the coercive voltage that scales with the applied gamma dose and depends on the electrode material. This work advances the understanding of the interaction between radiation and HfO₂-based ferroelectrics in order to probe the fundamental limits of radiation tolerance in this material.

9:15am AA1-WeM-6 Enhancement of Ferroelectric Phase Formation of HfO₂/ZrO₂ Nanolaminate Films by Tuning HfO₂ and ZrO₂ Thicknesses Using Atomic Layer Deposition, *Takashi Onaya, Y. Sakuragawa, K. Kita,* The University of Tokyo, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) thin films are typically fabricated by forming HfO_2/ZrO_2 nanolaminate films deposited by alternately depositing HfO_2 and ZrO_2 layers using atomic layer deposition (ALD). It has been reported that the remanent polarization of HfO_2/ZrO_2 nanolaminate films changed depending on each HfO_2 and ZrO_2 thickness [1]. However, it is still unclear how each HfO_2 and ZrO_2 thickness affect the formation of ferroelectric orthorhombic (O) phase. In this work, we studied the crystal structure of HfO_2/ZrO_2 nanolaminate films with various conditions using ALD.

A 10-nm-thick HfO_2/ZrO_2 nanolaminate film was deposited on a TiN/p-Si substrate by alternately depositing HfO_2 and ZrO_2 layers using ALD at 300°C. $Hf[N(C_2H_5)CH_3]_4$ and $Zr[N(C_2H_5)CH_3]_4$ precursors were used for HfO_2 and ZrO_2, respectively, and H_2O was used for an oxidant. The ALD cycle ratio was varied from HfO_2/ZrO_2=1/1 to 60/60 so that each HfO_2 and ZrO_2 thickness would be varied from 0.08 to 5 nm while keeping the total thickness of the nanolaminate film to 10 nm. Finally, post-deposition annealing was performed at 600°C for 1 min in a N_2 atmosphere. A 10-nm-thick HZO solid-solution film was also fabricated by ALD using a $Hf/Zr[N(C_2H_5)CH_3]_4$ cocktail precursor as a reference.

In grazing-incidence X-ray diffraction (GIXRD) spectra, all samples clearly showed the diffraction peak at ~30.7°, attributed to either O(111), tetragonal (T) (101), or cubic (C) (111) (O/T/C) phases. The peaks for HfO_2 and ZrO_2 are not distinguishable due to almost the same lattice constant. The O/T/C peak areas of the HfO_2/ZrO_2=6/6 and 12/12 films were ~1.4 times larger than that of the HZO solid-solution film, where each HfO_2 and ZrO_2 thickness was 0.5−1 nm (1−2 monolayers). On the other hand, the HfO_2/ZrO_2=1/1 and HZO solid-solution films showed similar O/T/C peak area, because Hf and Zr atoms could be uniformly mixed in the HfO_2/ZrO_2=1/1 film. In addition, the O/T/C peak area decreased by increasing ALD cycle ratio, such as the HfO_2/ZrO_2=20/20 and 60/60. We also found that the as-grown ZrO_2 film was already crystallized in O/T/C phases even without annealing, whereas the most of as-grown HfO_2 and HZO solid-solution films was amorphous [2]. Therefore, the ZrO_2 layers in HfO_2/ZrO_2 nanolaminate films should play a role to provide nuclei efficiently to enhance the O/T/C phase formation in the HfO_2/ZrO_2=6/6 and 12/12 films.

In conclusion, the O/T/C phase formation can be prompted by using HfO_2/ZrO_2 nanolaminate films with each HfO_2 and ZrO_2 thickness of 1−2 monolayers.

[1] J. Liao et al., IEEE Electron Device Lett. 40, 1868 (2019).

[2] T. Onaya et al., APL Mater. 7, 061107 (2019).

9:30am AA1-WeM-7 Investigating the Impact of Process Parameters on the In-plane Strain of Ultra-Thin $H-f_xZr_{1-x}O_2$ Films, *Florian Wunderwald,* Namlab, Germany*; B. Xu,* Namlab, China*; P. Vishnumurthy,* Namlab, India*; S. Enghardt,* TU Dresden, Germany*; K. Holsgrove,* Queen's University Belfast, UK*; A. Kersch,* University of Applied Sciences Munich, Germany*; T. Mikolajick, U. Schroeder,* Namlab, Germany

Since the development of Atomic Layer Deposition (ALD) 50 years ago, the technique has improved the deposition of thin films [1]. The first hafnium oxide processes were developed in the mid-1990s, and the material has been in mass production for semiconductor devices since 2007 [2, 3]. Interestingly, in the same year, T. Boescke discovered ferroelectricity in doped hafnium oxide thin films [4]. The finding of ferroelectricity in a fluorite-structured material, which is simultaneously compatible with semiconductor processing, has generated significant interest in their use for cutting-edge technologies such as non-volatile memory applications, neuromorphic computing, and AI applications [5]. To achieve the desired industrial properties of the material, which include high remnant polarization, high endurance, and high retention, understanding the impact of ALD processing on the later properties is crucial. In addition to that, the thickness scaling and behavior of ultra-thin $Hf_{-x}Zr_{1-x}O_2$ films are receiving more attention from the industry [5]. However, there is a lack of studies that review the impact of the single-stack engineering steps, such as atomic layer deposition (ALD), interface engineering, and annealing conditions, on one of the key factors: biaxial in-plane strain and its influence on ferroelectric phase formation in ultra-thin $H-f_xZr_{1-x}O_2$ films.

This study fills this gap and investigates the shortcomings mentioned above. To determine the biaxial in-plane strain, the lattice spacing was measured using the $sin^2\Psi$-method [6]. The results in Figure 2 show a clear increase in in-plane strain for thinner films, indicating a stronger impact of interfacial crystal lattice misfits, which can be confirmed by TEM measurements. Changes in strain lead to phase transitions for thinner films. To determine the different phases Gracing Incidence XRD (Figure 3) and EBSD (Figure 4) has been performed. For a deeper understanding and correlation, bipolar electric field cycling measurements were carried out to set the strain results in correlation with the electric switching field.

This study aims to enhance the knowledge of the influence of ALD process parameters on the in-plane strain in thin and ultra-thin $Hf_{-x}Zr_{1-x}O_2$films. The findings will provide a better understanding of processing and, thus, the establishment of $Hf_{-x}Zr_{1-x}O_2$films in non-volatile memory storage applications.

9:45am AA1-WeM-8 Thermal ALD IGO Channel Layer with High-thermal Stability (> 800 °C) for New Hybrid (Poly-Si/IGO) Vertical 3D NAND Application, *Su-Hwan Choi, J. Sim,* Hanyang University, Korea*; C. Park,* Hanyang University, Korea, Republic of Korea [], Republic of Korea*; Y. Song, J. Park,* Hanyang University, Korea

The oxide semiconductor (OS) channel materials represented by IGZO have been attracting attention from memory devices such as DRAM and NAND flash applications because of their outstanding properties, such as high mobility, low off-current, and excellent uniformity. Especially for the NAND flash memory, high field-effect mobility OS is proposed as the channel layer. However, OS channel NAND has problems, such as the inability to erase operations and poor thermal stability. To improve the disadvantages of OS channel NAND, we proposed a hybrid channel (HC, Poly-Si/OS) for V-NAND flash memory in which a poly-Si and an OS channel coexist for the remaining gate-induced-drain leakage (GIDL) erase scheme and high mobility, respectively. In this study, we adopt the atomic layer deposition (ALD) method for depositing the OS channel. The ALD has great advantages, such as excellent step coverage and sub-nanometer-scale thickness control. Especially for hybrid channel structures, high step coverage properties of OS deposition are crucial because the aspect ratio is increased by Poly-Si channel deposition. This is because the hole diameter of the V-NAND string is decreased by poly-si thickness, whereas the hole height is similar.

In this study, we adopt the IGO for the hybrid channel structure (poly-Si/IGO). The DBADMIn was adopted to deposit the InO, the mother material of IGO. As shown in **Fig 1 (a) and (b)**, the 250 °C deposited InO using ozone as a reactant easily crystallizes even at 3 nm thick with highly c-axis aligned Cubic (222) orientation, exhibiting superior electrical and stability properties. The TMGa was adopted to gallium doping for the InO channel using the super-cycle method. A thickness of IGO above 10 nm is needed to achieve high thermal stability after the post-annealing process at 800 °C for 3 hours because the thermal stability of IGO is related to crystallinity (**Fig 1 (c)**). The vertically structured HC NAND flash was successfully fabricated, as shown in **Fig 2**. The Schematic of the V-NAND flash memory structure for illustrating conventional poly-Si and the purpose of the hybrid-channel (HC) structure are summarized in **Fig 2(a)**. As shown in **Fig 3 (a)**, the GIDL current of HC channel NAND flash was achieved and confirmed as successfully operating the program and erase operation after the post-annealing process at 800 °C for 3 hours. We easily understand the conventional program, however, in the case of GIDL erase, through **Fig. 3(b)**, the proposed HC structure generates a band to band tunneling generation through a poly-Si channel, therefore the GIDL-assisted increasing channel potential can be confirmed through hole current generation.

ALD Applications

Room Hall 3D - Session AA2-WeM

Memory Applications: RRAM & Neuromorphic, MIM Capacitors

Moderators: Uwe Schröder, Namlab, **Seung-Yeul Yang**, Samsung

10:45am **AA2-WeM-12 Towards Neuromorphic Computing Using ALD Grown HfO$_2$ Based Memristive Devices**, *Christian Wenger,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany **INVITED**
Due to its advantages of massive parallelism, high energy efficiency, and cognitive functions, brain-inspired neuromorphic computing is attracting immense interest. As the basic unit cell for learning algorithms, the implementation of synaptic behavior into memristive devices is the key step toward neuromorphic computing.

Recent advances in the performance of resistive random access memory (RRAM) acting as memristive devices have led to a significant interest in neuromorphic applications. Although RRAM based memory arrays demonstrated excellent performance parameters, the variability is still a critical issue. Controlling this intrinsic phenomenon requires employing program-verify schemes. In this talk, an optimized scheme to minimize resistance state dispersion and to achieve reliable multi-bit operation is evaluated.

However, statistical variations can be tolerated in computing applications like neuromorphic networks. The synaptic behavior memristive devices can be evaluated by applying successive algorithms consisting of set or reset pulses. These algorithms can be used to study the synaptic functionality of memristive arrays.

Nevertheless, there is still a huge gap between the physical implementation and the verification of circuits and systems proposed for memristive devices. The first step, required to fill the gap, is the development of analog simulation tools, which are the base for the successful implementation of digital CMOS circuits with memristive elements. New designs and concepts need to be supported up by physical implementation and verification to be reliable. That means, new simulation tools for memristive devices have to address the following issues: device variability, cycling variability, data endurance, data retention as well as device switching speed. Meaning that memristive device models still have a long way to be completed.

11:15am **AA2-WeM-14 Novel Carbon-Doped HfO$_x$ Memristor with Born-ON Characteristics Synthesized via ALD/MLD Combined Technique**, *Minjong Lee, Y. Hong, J. Kim, D. Le, D. Kim,* University of Texas at Dallas; *R. Choi,* Inha university, Republic of Korea; *J. Rohan, G. Yeric,* Cerfe Labs; *J. Kim,* University of Texas at Dallas
Transition metal-oxide (TMO) materials are recognized as the most promising for memristive devices. The majority of TMO memristors require a one-time initialization step, during which a relatively large voltage induces filamentary switching. This forming process introduces challenges, including large overshoot currents under high voltage conditions [1]. Beyond typical memristive operations, including the initial forming process, the novel concept of a born-ON memristor generates universal non-polar switching in carbon-doped TMO films deposited by spin-on fabrication [2]. The introduction of additional defects to the pristine TMO film results in born-ON characteristics accompanied by excellent device yield and reliability. However, spin-on fabrication has a significant limitation as it is not compatible with CMOS process. In our previous presentation at the ALD/ALE 2023 conference, we demonstrated feasible born-ON characteristics by using a carbon-composited oxidant during the ALD process [3].

Herein, we extend the technical feasibility of previous work to demonstrate a super-cycle approach generating controllable HfOx film density and carbon concentration. Beyond typical HfOx film deposition using TDMA-Hf and H2O, we used ethylene glycol (EG) as an additional reactant for carbon doping. Within the super-cycle framework, we varied the 'm' cycles of the ALD process (TDMA-Hf/H2O) and the 'n' cycles of the MLD process (TDMA-Hf/EG). Notably, adjusting the ratio between the ALD and MLD processes resulted in HfOx film densities ranging from 4.5 to 9.4 g/cm3 (Fig. 1a). Furthermore, leveraging this super-cycle approach of ALD and MLD cycles provides control over the carbon rate, evident from the XPS profiles (Fig. 1b). The electrical characteristics of HfOx memristors were comprehensively investigated across various carbon concentrations (Fig. 2a). With an increase in carbon concentration to 10%, the set voltage decreases, and the initial leakage current closely aligns with OFF current, indicating a forming-free memristor. In devices with 15% carbon, we achieved born-ON memristive behavior. This device ensures reliable non-volatile memory operation with excellent endurance and retention properties (Fig. 2b). Our work marks a significant advance towards the development of novel forming-free TMO memristors within this controllable film density paradigm using super-cycle approach of ALD and MLD processes.

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[3] M. Lee et al., ALD/ALE 2023 (2023).

11:30am **AA2-WeM-15 Evolution of Structural Order in Doped Hafnia Thin Films by Atomic Layer Deposition for Emerging Device Applications**, *Mohammad Hassan Sultani, F. Cüppers,* Forschungszentrum Juelich GmbH, Germany; *A. Dippel, O. Gutowski,* Deutsches Elektronen Synchrotron DESY, Germany; *A. Besmehn, D. Müller, S. Hoffmann-Eifert,* Forschungszentrum Juelich GmbH, Germany
HfO$_2$-based thin films by atomic layer deposition (ALD) are widely used in emerging electronic devices. Monoclinic and tetragonal structures serve as high-k dielectric in field effect transistors (FET). Films with ferroelectric orthorhombic structures, often achieved by doping, enable ferroelectric FETs. Further, thin films of HfO$_2$ form the switching layer in resistive random-access memories (ReRAM) for new neuromorphic computing architectures. Due to limitation of the thermal budget in back-end-of-line to about 450°C, an amorphous state of the HfO$_2$ layer after full chip fabrication is essential for high device-to-device reproducibility. For a deeper understanding of the optimum design of emerging devices based on ALD HfO$_2$ films, it is crucial to describe the nature of the amorphous material and to control the crystallization process and the resulting phase by heterovalent and homovalent doping.

The present study investigates the structural properties of thin films from HfO$_2$ doped with Al, Si, and Ti. The films at a total thickness of 30 nm were grown in a FlexAL™ system at 250°C heater temperature using oxygen plasma as the counter reactant. Tetrakis(ethylmethylamido)hafnium, trimethylaluminium, Bis(tertiary-butylamino)silane, and tetrakis(dimethylamino)titanium served as metal precursors. Effective dopant concentrations between 2 and 10 at% were realized by the growth of nanolaminates of n-times (x cycles HfO$_2$ - y cycles MO$_x$ – x cycles HfO$_2$)(with M=Al, Si, Ti). The laminate structures after growth and crystallization were characterized by X-ray reflectivity and by time-of-flight secondary ion mass spectroscopy. The local structure of the amorphous layers was probed by high-energy X-ray scattering at grazing incidence and pair distribution function analysis. Further, in-situ thermal treatment in vacuum allowed to study the crystallization process of the different films in detail. Crystallized films were analyzed by high-resolution grazing-incidence X-ray diffraction. The measurements were performed at PETRA-III storage ring at DESY

The results will be discussed with special emphasis on the effects of the dopant element, the laminate sequences, the effective doping concentration on the local structure of as-grown films, on the crystallization behavior, and on the crystalline phase obtained after annealing. Results of this study can enhance the understanding of the thin films' local structure and the crystallization process and thereby can support the optimization of material's and process' design for the various applications of HfO$_2$ thin films in emerging devices for energy-efficient next-era computing applications.

11:45am **AA2-WeM-16 ALD HfZrO2 Films from Ferroelectric to High-k Applications**, *Alessandra Leonhardt,* ASM, Finland; *R. Ramachandran,* ASM, Belgium; *M. Surman,* ASM, Finland; *R. John, F. Tang, M. Balseanu,* ASM; *A. Illiberi,* ASM, Belgium
HfO2 based ferroelectric (FE) materials have gained tremendous attention as a potential candidate for memory applications such as FeFET and FeRAM. Since its first demonstration as a FE material [1], immense research has been done to circumvent the challenges such as scalability, increasing the remnant polarization (Pr), and improving endurance. Among others, Zr-doped HfO2, HfZrO$_2$ is being intensively studied due to its compatibility with complementary metal oxide semiconductor (CMOS) processing and excellent scalability. ALD has been the technique of choice for the deposition of those films, due to the high conformality, high film quality and simplicity of tuning the composition. HfZrO$_2$ has excelled in this field, with high polarization, high endurance and retention. Those properties

were still further improved by the addition of dopants such as La, which resulted in the record high 2Pr for films fabricated by ASM and imec using metalorganic precursors [2].

In this presentation we take ALD $HfZrO_2$ one step forward, and describe how, with the addition of suitable dopants, the ferroelectricity can be modulated in a broad range, and how this can be incorporated in applications where high dielectric constants are desired. We discuss the use of Al dopants in $HfZrO_2$ and explore the relationship between film composition and electrical properties, discussing the physics of ferroelectricity and high dielectric constant. Thin Al:$HfZrO_2$ films show significant modifications in their dielectric properties with respect to pure $HfZrO_2$. Low Al doping levels initially boost the capacitance, while higher levels results in CV peak shifting which leads to a quasi-flat CV behavior at 5% Al doping. This is consistent with the model of dopants with small atomic radius promoting tetragonal phases inside the (initially orthorhombic) $HfZrO_2$ lattice [3]. This results in high dielectric constant at relevant operation voltages e.g. k>40 @ -1.2V for 6-7nm films, which is in line with future high-k applications.

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ALD Applications
Room Hall 3E - Session AA3-WeM

Other Emerging Applications

Moderators: Sumit Agarwal, Colorado School of Mines, **Parag Banerjee**, University of Central Florida

10:45am **AA3-WeM-12 Tunable Superconducting Nb$_x$Ti$_{1-x}$N by Fast Plasma-enhanced ALD for Quantum Applications**, *Silke Peeters, L. Nelissen,* Eindhoven University of Technology, Netherlands*; D. Besprozvannyy,* Oxford Instruments Plasma Technology, UK*; M. Verheijen,* Eindhoven University of Technology, Netherlands*; M. Powell, L. Bailey,* Oxford Instruments Plasma Technology, UK*; E. Kessels,* Eindhoven University of Technology, Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, UK

Superconducting films ranging from a few to hundreds of nanometers are at the basis of a wide range of quantum devices, and are therefore key in advancing quantum technology to an era of widespread utility. The further development of quantum technologies hinges on improvements in materials and their interfaces. With its atomic-scale growth control, plasma-enhanced ALD (PEALD) could become an enabling technique for the growth of superconducting thin films with high-quality interfaces. High-throughput processes will facilitate the growth films beyond 100 nm, broadening the application perspective for ALD of superconducting films.

We demonstrate PEALD of superconducting Nb$_x$Ti$_{1-x}$N films ranging from 5 to 100 nm thickness at a high throughput of >50 nm/hour on the Plasma Pro ASP system. The depositions consist of NbN and TiN supercycles using the TBTDEN and TDMAT precursors and an Ar/H$_2$/N$_2$ plasma at a table temperature of 320 °C. The RF-driven remote capacitively coupled plasma source is combined with RF substrate bias functionality allowing for ion-energy control.

The Nb$_x$Ti$_{1-x}$N films show critical temperatures of superconductivity from 3 K at x=0 to 13 K at x=1 for 25 – 50 nm films. High film quality is confirmed by low O impurity contents ~ 5 at.% or lower and room-temperature resistivities increasing with Nb content from 160 μΩ cm (41 nm TiN) to 284 μΩ cm (25 nm NbN). Accurate composition control of Nb$_x$Ti$_{1-x}$N is demonstrated from x=0 to x=1, with the C content increasing from 5 at.% to 16 at.% and the N content correspondingly decreasing from 48 at.% to 36 at.%. EDX mapping confirms homogeneous mixing of Ti and Nb, and XRD measurements show all prepared films are fcc polycrystalline. Tuning of the ion energy indicates a stable composition, while the crystallinity and conductivity can be influenced. TEM imaging of the most conductive 49 nm Nb$_{0.5}$Ti$_{0.5}$N film reveals a disordered polycrystalline film in agreement with XRD measurements. A relatively high sheet kinetic inductance of 24 pH/sq is found for 38 nm film thickness. In addition to lowering resistivity, substrate biasing provides the ability to enhance film disorder, making these films attractive for applications such as microwave kinetic inductance detectors. The high throughput and tunability of the Nb$_x$Ti$_{1-x}$N deposition process puts forward PEALD as a promising technique to tackle material challenges in quantum technologies.

11:00am **AA3-WeM-13 Atomic Layer Deposited Metal Nitrides (TiN and InN) and Metal Semiconductor Heterojunctions for Quantum Applications**, *Neeraj Nepal, J. Prestigiacomo, M. Sales, P. Litwin, T. Growden, V. Wheeler,* US Naval Research Laboratory

Direct integration of III-N semiconductors with superconductors are beneficial for quantum technologies such as superconducting qubits, secure quantum communications, and superconducting radio-frequency circuits [1]. To-date direct integration has been achieved using III-N/NbN grown at >600 °C [1]. Atomic layer deposition (ALD) provides a path towards integration at lower temperatures with wafer scale uniformity, conformality and subatomic thickness control. Titanium nitride (TiN) is a favorable, superconductor (T$_c$ ~5.6 K [2]) to integrate with III-N materials. In fact, ALD TiN has been used as a Schottky gate metal in III-N devices for improved electrical and thermal performance [3]. Also, kinetic inductance is one of the highest in TiN [4] and increases with decreasing thickness. High quality InN semiconductor with high carrier concentration has been demonstrated by ALD [5]. Thus, integrating high quality, crystalline ALD deposited TiN metal with InN semiconductor could provide metal-semiconductor heterojunctions (HJ) for various quantum applications.

ALD TiN and InN films (40 nm), were deposited as single and bilayer structures on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor. TDMAT and TMI precursors were used to grow TiN and InN, respectively. An Ar/N$_2$ plasma at 300W was used for both layers. ALD process windows were monitored and optimized on Si substrates using *in-situ* ellipsometry and *ex-situ* characterizations. Both materials were determined to have a common ALD window at 250 °C allowing bilayers to be deposited at these temperatures with abrupt interfaces.

40 nm TiN films grown on c-sapphire and resistive Si(100) exhibited a T$_c$ of 3.85 K and 3.45 K, respectively. This is similar to previously reported 50 nm TiN films on resistive Si with a T$_c$ of 4.05 K [4]. XRD revealed a more crystalline TiN film on sapphire than Si, which could account for the higher T$_c$ measured. ALD InN films exhibited a high electron carrier concentration of ~4x10^{20} cm^{-3}. Bilayer semiconductor-superconductor HJ of 40 nm TiN/40 nm InN on and 40 nm InN/40nm TiN were then deposited on sapphire at 250 °C. XRD shows that individual layers in these HJ are crystalline with both InN (0002) and Ti(111) peaks present. Detailed ALD growth and characterization results will be presented for all layers and discussed in context of use in quantum applications.

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11:15am **AA3-WeM-14 Ceramic Thin-Film Composite Membranes with Tunable Subnanometer Pores for Molecular Sieving by Atomic Layer Deposition**, *X. Zhou,* Yale University*; R. Shevate, A. Mane, **Jeffrey Elam**,* Argonne National Laboratory*; J. Kim, M. Elimelech,* Yale University

Membranes with tunable, sub-nanometer pores are needed for molecular separations in applications including water treatment, critical mineral extraction, and recycling. Ceramic membranes are a promising alternative to the polymeric membranes typically used in such applications due to their robust operation under harsh chemical conditions. However, current fabrication technologies fail to construct ceramic membranes suitable for selective molecular separations. In this presentation, we describe a ceramic thin film composite (TFC) membrane fabrication method that achieves sub-nm pore size control using atomic layer deposition (ALD) by incorporating a molecular-scale porogen. By co-dosing alkyl alcohols along with the H$_2$O coreactant during Al$_2$O$_3$ ALD, we incorporate alkoxide species in the film which create a continuous network of pores upon calcination. Varying the alkyl alcohol (methanol, ethanol, isopropanol) tunes the pore size. We use Fourier transform infrared absorption spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy to elucidate the surface chemistry and growth during the alcohol-modulated ALD as well as the subsequent pore formation. We evaluate the transport and separations properties of the ALD TFC membranes using a two-chamber diffusion cell with aqueous salt solutions. We measured a remarkable enhancement in the transport of Cl$^-$ compared to SO$_4^{2-}$ (8.6 times faster) matching the selectivity of state-of-the-art polymer membranes. We attribute this selectivity to the dehydration of the large divalent ions within the subnanometer pores. In addition, permeation studies using neutral adsorbates revealed average pore sizes of ~7Å, 13Å, and 19Å for ALD TFC

membranes prepared using methanol, ethanol, and isopropanol, respectively. This work provides the scientific basis for the design of ceramic membranes with subnanometer pores for molecular sieving using ALD.

11:30am AA3-WeM-15 Recent Developments and Emerging Applications in Atmospheric-Pressure Atomic Layer Deposition of High-Porosity Materials, *M. Chen,* TU Delft, China*; M. Nijboer, A. Kovalgin, A. Nijmeijer,* University of Twente, The Netherlands*; F. Roozeboom,* University of Twente and Carbyon B.V., Netherlands*; **Mieke Luiten-Olieman**,* University of Twente, The Netherlands

Atomic layer deposition (ALD) is a widely recognized technique for depositing ultrathin conformal films with excellent thickness controlat Ångström or (sub)monolayer level. Atmospheric-pressure ALD is an upcoming ALD process option with a potentially lower reactor ownership cost.

We will present a comprehensive overview of the recent applications and development of ALD applications exclusively working at atmospheric pressure [1]. Spatial ALD (sALD) has been recently introduced for the commercial surface passivation and encapsulation in the large-area production of solar cells, and for the production of 2D displays, in particular organic light-emitting diode (OLED) displays. Atmospheric-pressure temporal ALD (tALD) has found its route for new emerging applications such as high-porosity particle coatings, functionalization of capillary columns for gas chromatography, and membrane modification in water treatment and gas purification. The challenges and opportunities in achieving highly conformal coatings on porous substrates by atmospheric-pressure ALD will be discussed.

Typically, each application often requires its own optimized reactor design [1]. For the application of tuning and functionalizing nanopores in tubular ceramic nanofiltration membranes, we will present a new tubular reactor design [2]. In this design, the reactor wall is formed by the industrial tubular ceramic membrane itself, and carrier gas flows are employed to transport the precursor and co-reactant vapors to the reactive surface groups present on the membrane surface, see Fig. 1. The layer growth for atmospheric-pressure ALD, in this case, proceeds similarly to that for state-of-the-art vacuum-based ALD. Moreover, for membrane preparation, this new reactor design has three advantages: i) monolayers will be deposited only at the outer pore mouths rather than in the entire bulk of the porous membrane substrate, resulting in reduced flow resistances for liquid permeation; ii) an *in-line* gas permeation method was developed to monitor the layer growth in the pores during the deposition process, allowing more precise control over the finished membrane (see Fig. 2), and iii) expensive vacuum components and cleanroom environment are avoided. This opens up a new avenue for commercial ceramic membrane functionalization with nano-scale precision by using ALD at atmospheric pressure.

Literature references:

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11:45am AA3-WeM-16 Modulation Acceptor Doping of Silicon Nanowires using a SiO₂-shell doped with ALD Metal Oxide Monolayers, *Daniel Hiller,* Institute of Applied Physics (IAP), TU Bergakademie Freiberg, Germany*; S. Nagarajan,* Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden, Germany*; I. Ratschinski, S. Shams,* Institute of Applied Physics (IAP), TU Bergakademie Freiberg, Germany*; M. Venzke,* Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany*; P. Hönicke,* Helmholtz-Zentrum Berlin (HZB), Berlin & Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany*; T. Mikolajick,* Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden & Institute of Semiconductors and Microsystems, TU Dresden, Germany*; J. Trommer,* Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden, Germany*; D. König,* Integrated Materials Design Lab (IMDL), Australian National University (ANU), Canberra, Australia

Silicon nanowires (Si NWs) or nanosheets are the building blocks for future transistors and efficient doping processes are inevitable for conductivity. Yet, NWs suffer from severe difficulties with efficient impurity doping due to a multitude of physical and technological problems when the diameters are reduced to a few nanometers: diffusion, dielectric and quantum confinement, statistics of small numbers, etc. Junctionless NW-transistors (JNTs) in particular require high conductivities. However, high impurity dopant concentrations are accompanied by a severely decreased mobility, which in turn implicates the need for higher operation voltages and

increased electrical energy dissipation into heat. Therefore, alternative doping methods are desirable to separate the dopant atoms from the doping-induced free carriers.

Here, we present a novel modulation doping approach for Si NWs. According to results from density functional theory (DFT) calculations [1,2], we use Al- or Ga-doped SiO₂ as a shell around Si NWs. The trivalent group-III impurities incorporated into the tetravalent SiO₂ network form unoccupied acceptor states with an energy level located below the Si valence band edge (cf. Fig. 1). Such induced acceptor states can capture electrons from Si, creating free holes as majority charge carriers in the process [1-5].

Experimentally, the Al- or Ga-doping of SiO₂ is realized by ALD to form (sub-)monolayers of Al₂O₃ or Ga₂O₃ on an ultra-thin tunnel-SiO₂ and a subsequently deposited capping layer of SiO₂ or HfO₂. Crucial details of the Al/Ga-deposition on a dry-thermal oxide surface during the initial ALD-cycles are obtained via synchrotron-based reference-free grazing incidence X-ray fluorescence spectrometry (GIXRF) [6].

In this presentation, we furthermore demonstrate that Si NWs with modulation-doped SiO₂ shells exhibit up to 6 orders of magnitude lower electrical resistances as compared to NWs with undoped SiO₂-shells, as shown in Fig. 2 [7,8].

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ALD Fundamentals
Room Hall 3A - Session AF1-WeM

Growth and Characterization: High Aspect Ratio/High Surface Area/Powder ALD and Characterization of ALD Films

Moderators: Noureddine Adjeroud, Luxembourg Institute of Science and Technology (LIST),, **Viljami Pore**, ASM

8:00am AF1-WeM-1 Conformality of Ternary Oxides by Spatial ALD: Monte Carlo Simulations and Experimental Study, *Mike van de Poll, S. van der Heijden, P. Poodt, E. Kessels, B. Macco,* Eindhoven University of Technology, Netherlands

Conformal film growth is one of the key merits of ALD and essential for many applications. The conformality of binary oxide depositions using a simple AB-process has been thoroughly examined in the past and is well understood. Although materials containing three or more elements have been conformally deposited before in 3D-structures, fundamental understanding is still limited. This is especially the case for spatial ALD (s-ALD), which is promising for high-volume low-cost applications. In this work, we investigate the conformality of atmospheric-pressure s-ALD deposited ternary oxides, both through modeling and experiments.

A significant influence of the precursor dosing method (i.e., dosing the metal precursors in separate cycles within a supercycle versus co-injecting both metal precursors simultaneously) on the conformality was demonstrated using a Monte Carlo model. The supercycle method generally grants a large degree of control over the film stoichiometry because of the fact that the precursor doses can be tuned separately. To obtain films with invariable stoichiometry with respect to position in the trench, the doses should be tuned either such that either full step coverage is reached, or such that the penetration fronts of both precursors overlap. Controlling the composition is more challenging for Co-injection. Modeling results highlight the importance of many different aspects, such as precursor partial pressure, diffusivity, and sticking probability.

The modeling results were confirmed experimentally for both dosing methods by spectroscopic ellipsometry and XPS. Additionally, experimental results show the importance of precursor–precursor interactions at the surface during co-dosing. Al-doped ZnO and AlZnO were deposited in lateral high-aspect-ratio (LHAR) test chips (PillarHall™ by Chipmetrics Ltd)

using DMAI, DEZ, and water. Co-injection resulted in two distinct regions: an Al-rich region at the start of the trench, followed by a Zn-rich region deeper in the trench. A detailed study revealed that DMAI displaces DEZ molecules bound to the surface, resulting initially in primarily AlO_x growth, followed by ZnO growth deeper in the trench where DMAI is depleted. Precursor displacement can potentially play a role for many other co-injection processes depending on the reactivity of the precursors.

This study into the different dosing methods of s-ALD has shown which aspects are important for conformal deposition and enables the deposition of high-quality ternary oxides in high-aspect-ratio structures.

8:15am AF1-WeM-2 Reusable Macroscopic HAR Test Kit Enabling Fast, Routine Characterization of Film Conformality, *Jesse Kalliomaki, I. Manninen, J. Järvilehto,* Applied Materials, Finland

A defining feature of atomic layer deposition (ALD) is conformality, which has made it an invaluable tool in several industries. However, the testing film growth in high-aspect-ratio (HAR) structures has thus far been a laborious, slow, and costly endeavor, involving manual analysis of specialized nanostructures [1]. This limits the conformality studies during ALD process development.

This approach also neglects another strength ALD offers, scalability. ALD can coat macroscopic objects conformally as well as the microscopic. However, conformality tests carried out on a microscopic scale often led to overestimation of the film penetration depth at half-thickness (PD50) on macroscopic HAR objects [2], failing at the intended purpose of the ALD film.

Our work introduces a novel approach to tackle the issue of cost and scalability: a reusable HAR-test device comprising a wafer-sized annular metal disk with radial grooves of varying height (50-900 μm) extending outwards (Fig 1a). When placed on a wafer, closed lateral tunnels with varying aspect ratios are formed. After deposition, growth pattern is revealed by removing the disk (Fig 1b), easily accessible using wafer-scale instruments. Due to the macroscopic size of the pattern, low resolution techniques, such as ellipsometry or even measurement using a ruler, can be used to obtain useful results. This feature was leveraged to boost process development efficiency by varying a process parameter in steps during a deposition. This resulted in a staircase profile, comprised of characteristic PD50s of the varied parameter (Fig. 1c). For example, a TEMAHf-H2O deposition using TEMAHf pulse times of 1.0, 2.0, 2.7 & 3.0 s, resulted in PD50s of 16, 20, 22 & 23 mm, respectively, in a tunnel with a height of 240 μm. Data from 12 tunnels was combined to form the HAR Growth Constant (HGC), describing how the process scales to HAR features with any hydraulic diameter within the same flow regime.

This invention (patent pending) enables routine conformality testing during process development in a cost-effective and timely manner - facilitating further exploration of experimental conditions.

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8:30am AF1-WeM-3 Superconformal ALD Using a Heavy Inert Diffusion Additive, *Arun Haridas Choolakkal, P. Mpofu, P. Niiranen, J. Birch, H. Pedersen,* Linköping University, Sweden

The self-limiting surface chemistry of ALD routinely allows perfectly conformal, i.e., a step coverage of 1, film deposition. However, achieving superconformal deposition, i.e., a step coverage above one, with thicker film in the bottom of a recessed feature than in the top, has remained elusive in ALD, we will here show that it is possible. We recently showed how a CVD process for boron carbide using triethyl boron as single source precursor can be perfectly conformal by adding a co-flow of Xe.[1] Here, we expand on this concept by using Kr as diffusion additive in thermal ALD of AlN from trimethyl aluminum (TMA) and ammonia (NH_3).

We observe that the step coverage in 16:1 aspect ratio feature increased from 1 to 1.4 with the addition of Kr to the ALD process. The deposition depth observed from initial depositions conducted in lateral high-aspect-ratio (LHAR) chips with 500 nm gap height shows no significant change with Kr addition and it remainedat 42 μm.

The rationale behind this is the competitive co-diffusion of mainly the lighter NH_3 (17 amu) and Kr (83.8 amu) during every other half-cycle. The higher sticking probability of TMA ensures a chemisorbed layer up to 42 μm depth in the LHAR structure, limited by the influx of the given TMA dose. Kr, with a lesser mass difference with TMA (72 amu), does not provide a notable competitive advantage during co-diffusion. This means that NH_3

molecules are pushed down to the trench bottom, resulting in dilution at the openings of the high-aspect-ratio feature. This dilution prevents the surface saturated half-reaction at the openings while achieving an excess NH_3 concentration at the trench bottom, ensures surface saturated half-reactions at the bottom surfaces.

Reference:

A. H. Choolakkal et al. Competitive co-diffusion as a route to enhanced step coverage in chemical vapor deposition. *ChemRxiv* **2024**: doi:10.26434/chemrxiv-2024-nlf00

8:45am AF1-WeM-4 Ald of Alumina-Silica Multilayers on Carbon Microfiber Fabrics: Microstructure and Potential as Refractory Oxygen Diffusion Barriers, *Elise des Ligneris, D. Samélor,* CIRIMAT-INPT, France*; A. Sekkat,* CNRS, France*; C. Vahlas,* CIRIMAT-INPT, France*; B. Caussat,* CNRS, France

Provided that the sensitivity of carbon fibers (CFs) to thermal oxidation above 400 °C is tackled, CFs could then be used as reinforcement in high temperature composites, microwave absorption materials or thermal insulators in extreme environments [1, 2]. Indeed, CFs are not subjected to creep with increasing temperature, and exhibit even higher elongation modulus, contrary to ceramic microfibers such as SiC or boron-doped alumina [1, 2]. Rather than protecting a carbon macro-object, this study makes use of ALD for the deposition of a refractory oxygen diffusion barrier layer (OBL) on the surface of CFs (7 μm diameter) entangled within a woven fabric [1, 2]. While ALD of alumina-silica barrier layers was previously reported [3], the deposition of silica-based thin films on CFs have long been considered a challenge. Indeed, the oxidation-sensitive nature of CFs does not bode well with the thermal oxidative conditions associated with common protocols of silica ALD [3]. Nonetheless, the use of a catalytic ALD process illustrated in Scheme 1 enabled for the deposition of amorphous alumina-silica bilayers from 445 K using trimethylaluminium (TMA) and tris(*tert*-pentoxy)silanol (TPS) [2]. Amorphous alumina ALD was achieved below 120 °C using TMA and water [1]. The sequence of alumina low temperature ALD and alumina-silica catalytic ALD allowed for the deposition of alumina-silica laminates of tunable thicknesses on CFs, as presented in Figure 1[1, 2]. A CF-alumina interface prevented from carbon diffusion within the coating, while the fluid phase of silica could fill voids induced in part by alumina crystallisation. This study then focused on the compounds formed at the alumina-silica interface, in a trial to reach a three-dimensional structured coating, containing a crystalline mullite structure oriented parallel to the carbon substrate, and thus limiting events of intra-delamination.

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9:00am AF1-WeM-5 Pillarhall Lateral High Aspect Ratio Assisted Unveiling of Secondary Growth Front and Background Reaction Mechanism in Atomic Layer Deposition, *A. Philip,* Chipmetrics Ltd, Finland*; S. Elliott,* Schrödinger, Germany*; Jussi Kinnunen,* Chipmetrics Ltd, Finland*; A. Mirhamed,* Park Systems GmbH, Germany*; M. Zaheer, M. Utriainen,* Chipmetrics Ltd, Finland

The 3D vertical scaling trend in nanoelectronics necessitates high-aspect ratio (HAR) features and conformal ultra-thin films, crucial for the semiconductor industry today. The lateral high aspect ratio (LHAR) test structure and measurement method is a unique test vehicle for characterizing the conformality for the 3D thin films. The unique feature of LHAR is the ability to quantify the conformality for both ALD and CVD processes. PillarHall® LHAR4 test chips enable accurate and repeatable film penetration depth (PD) profile measurements which help to predict and quantify the step coverage in any HAR features. In the current research we are showing another important aspect of these LHAR beyond the already existing applications. Utilization of LHAR in understanding the reaction mechanism of ALD process especially in 3D structures is the major highlight of the current research. We reveal a secondary reaction front (ultra-thin layers, Figure 1) for the TMA+H2O thermal ALD process with the support of LHAR , contrast SEM and imaging ellipsometry techniques. The merit of

using imaging ellipsometer is that beyond visualizing the second front, it also facilitates the measurement of film thickness within the second front region. We checked the process at two different deposition temperatures (125°C and 300°C) and with different combinations of pulsing and purging lengths to investigate the influence of these parameters on the observed secondary growth front. The observation of secondary growth front for both temperatures unambiguously ruled out the deposition temperature influence on the observed feature. To investigate the possible mechanistic reasons for the secondary growth front, we have carried out microkinetic modelling of ALD cycles over a range of combinations of precursor pressures, simulating the situation at various cavity depths. As expected, high pressure of both precursors leads to high growth rates up to the primary growth front. At the lower pressures that are present further into the cavity, the model predicts much lower growth rates, along with an increase in the sticking coefficient of TMA (Figure 2). As the depth of a growth front scales with the square root of the sticking coefficient [1], the low-pressure growth front should therefore be deeper than the high pressure one, which matches the experimental observation. Our results indicate that the formation of the second front results from the presence of multiple reaction mechanisms, which are otherwise challenging to distinguish.

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9:15am **AF1-WeM-6 Helium Ion Microscopy on ALD Thin Films**, *Sami Kinnunen,* University of Jyväskylä, Finland*; E. Alakoski, T. Laine,* JAMK University of Applied Sciences, Finland*; T. Sajavaara,* University of Jyväskylä, Finland

Scanning electron microscopy (SEM) is routinely used to image thin nanoscale features such as thin films. Helium ion microscopy (HIM) is in many ways a very similar imaging method with few key differences. In HIM helium ion beam is used to scan the sample and back scattered electrons are detected. In addition to excellent resolution and depth-of-field, charging of insulating samples is easily counteracted with electron flood gun and no extra conductive coating is needed. It is also possible to use neon beam to mill material or fabricate patterns. On the other hand, the minimal generation of x-rays makes elemental analysis more complicated compared to SEM.

In this work we present examples of HIM at the University of Jyväskylä related to ALD and thin film research. For example, imaging insulating cellulose fibers (Fig. 1 a) or packaging materials coated with non-conducting thin films are regularly studied without any special sample preparation. We also show how HIM has been used as a focused ion beam (FIB) tool by changing the incident beam from helium to neon. This can be used, for example, to reveal the cross-section of the ALD film on a substrate (Fig. 1 b). We also show how HIM-based ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) can be used for elemental imaging with high spatial resolution and discuss the limitations of the technique at its current state.

9:30am **AF1-WeM-7 Understanding the Amorphous Structure of Al- and Zn- Doped TiO_2 with an Automated 4D-STEM Analysis Pipeline**, *Andreas Werbrouck, N. Paranamana, X. He, M. Young,* University of Missouri-Columbia

Titanium oxide is an ALD staple. It finds uses in microelectronics, (photo) catalysis and lithium-ion-based energy storage. One of the reasons for its attractiveness is the possibility to tune the functional properties by means of the structure: e.g. the conductivity of the material changes by means of doping and/or phase selection through annealing (anatase or rutile).

Amorphous TiO_2 is subject to similar effects. Small concentrations of impurities (e.g. dopants or precursor ligands) may have a large impact on the final structure. Similarly, subtly different structures may arise at the substrate-film or film-vacuum interface. This will affect the functional properties of the films. Due to the difficulty characterizing the nature of the amorphous phase, such differences are easily overlooked. Hence, it is necessary to develop spatially resolved, structural characterization techniques for both crystalline and amorphous materials.

In this work, we report on a 4D-scanning transmission electron microscopy (4D-STEM) investigation of the amorphous structure of undoped and doped TiO_2 as deposited with $TiCl_4$ and water, with $AlMe_3$ and $ZnEt_2$ as precursors for the doping. 4D-STEM measurements allow to investigate and map material structure at the nanoscale in a TEM: 2D diffraction data is available for every recorded pixel and can be combined with co-located Energy-

Dispersive X-ray Spectroscopy (EDS) data to match structures and compositions.

The large volume of data and the complexity of diffraction analysis makes manual processing of 4D-STEM data prohibitively slow. To address this, we developed an automated workflow for analyzing 4D-STEM data. This workflow is cast as a Directional Acyclic Graph (DAG). First, the 4D data is split into spatially mapped crystalline and amorphous components. Then, non-local averaging and non-negative matrix factorization distill the amorphous data into a low number of higher-quality pair distribution functions (PDFs). Finally, these can be structurally refined using reverse Monte Carlo (RMC) fitting and molecular dynamics (MD).

This automated approach greatly reduces the amount of time and effort necessary to interpret the data in a meaningful way. Specifically for TiO_2, we clearly observe how even a low level of Zn, Al and Cl impurities profoundly alter the amorphous structure. Through this effort, a better understanding of the as-deposited, amorphous material is gained, which can then serve as a stepping stone to study and engineer more advanced dielectrics, catalysts and electrode interfaces.

9:45am **AF1-WeM-8 Non-Destructive Characterization of ALD Thin Films Using Angle-resolved XPS and Structure Modeling**, *K. Artyushkova, N. Biderman,* **Wolfgang Betz,** Physical Electronics USA

A powerful tool for surface and interface analysis: X-ray photoelectron spectroscopy (XPS) has long been a trusted technique for analyzing the chemical composition of thin layers and interfaces, offering a non-destructive approach to unlocking valuable information. Angle-resolved XPS (AR-XPS) builds upon this foundation, leveraging the power of tilted measurements to determine the composition and thickness of multilayered films, reaching depths of up to 5-10 nanometers below the surface.

Conventional structure modeling algorithms applied to AR-XPS data rely on the assumption of uniform, discrete thin film growth. This approach presents significant limitations for accurate thickness determination when analyzing films with complex morphologies: pinholes, island growth, and non-uniform coverage which are particularly observed in atomic layer deposition (ALD) processes.

Structure modeling package *Strata*PHI goes beyond the limitations of conventional ARXPS data modeling for multilayered films. Its fractional coverage mode tackles non-uniform island morphologies typically seen in early ALD stages. This talk highlights *Strata*PHI's capabilities, including layer coverage and accurate thickness even for non-uniform layers.

By employing the microprobe X-ray spot of PHI XPS instruments, capable of analyzing areas ranging from as small as 5 µm in diameter and as large as 1mm x 200 µm, AR-XPS measurements can be used to assess thickness and coverage variations across multiple length scales providing deeper insights into growth mechanisms.

ALD Fundamentals
Room Hall 3A - Session AF2-WeM

Growth and Characterization: Low Temperature ALD
Moderators: John Conley, Oregon State University, **Henrik Pedersen**, Linköping University, Sweden

10:45am **AF2-WeM-12 Low-Temperature ALD of Metallic Cobalt for 3D Structures**, *Mathias Franz, L. Kaßner,* Fraunhofer ENAS, Germany*; C. Thurm,* University of Technology Chemnitz, Germany*; X. Hu,* Fraunhofer ENAS, University of Technology Chemnitz, Germany*; M. Daniel,* scia systems GmbH, Germany*; F. Stahr,* Forschungs- und Applikationslabor Plasmatechnik GmbH, Germany*; S. Schulz,* Fraunhofer ENAS, Center for Microtechnologies (ZfM), University of Technology Chemnitz, Germany

Atomic Layer Deposition (ALD) of metallic films is a broad and ongoing topic of research. The conformal deposition of metallic cobalt is relevant for modern interconnects[1], seed layers for electroplating[2], and antibacterial coatings[3]. One of the essential process parameters is the deposition temperature. Here, we present the development of a low temperature ALD process for the deposition of metallic cobalt on integrated 3D structures in silicon substrates.

We base our process development on a set of previously developed precursors of the form $[Co_2(CO)_6(RC≡CR')]$ published by Georgi et al.[4]. We evaluated a set of these precursors for ALD using density functional theory (DFT) calculations. According to these calculations the precursor $[Co_2(CO)_6(HC≡CC_5H_{11})]$ was identified as the most favourable precursor for deposition via ALD. It adsorbs with remaining $(HC≡CC_5H_{11})$ group which can

be easily removed by use of activated hydrogen. The process development was done on a novel *scia Atol 200* reactor. The depositions took place on 200 mm Si wafers with a preliminary SiO_2 layer of 100 nm thickness. The precursor was evaporated via the bubbling method. A full ALD cycle consists of a cobalt precursor pulse, an Ar purge, an H_2 plasma pulse, and a second Ar purge. The deposited cobalt films were analysed by *in-vacuo* ellipsometry to determine in-line the film growth rates. Figure 1 shows the growth per cycle in the temperature range from 35 °C to 125 °C showing the ALD window for this process within the range of 50 °C to 110 °C.[5] The process was optimised regarding pulse and purge duration times to ensure stable saturation conditions. *Ex situ* measurements with XPS confirm that cobalt is in metallic state. The optimised ALD process has been applied to silicon trench structures. Figure 2 shows a SEM image of cobalt deposited to the sidewalls of a silicon trench.

We demonstrated the successful development of a low temperature ALD process for metallic cobalt. This process was successfully applied to 3D structures.

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11:00am AF2-WeM-13 Towards Deposition of Metallic Molybdenum Films from Molybdenum Hexacarbonyl in a Process Involving an Intermediate ALD Step and Subsequent Reduction, *Kees van der Zouw, M. Sturm, T. Aarnink, A. Kovalgin,* University of Twente, the Netherlands

Atomic layer deposition (ALD) is expected to be essential for future CMOS back-end-of-line (BEOL) applications. Due to its electrical and thermal properties, molybdenum (Mo) is among the metals that have gained significant interest [1]. The research into ALD of metallic Mo has been limited to halide-based processes [2-5], in which corrosive byproducts like hydrogen fluoride or hydrogen chloride can be formed. A process for Mo ALD from a metalorganic precursor remains to be identified. This work investigates the feasibility of Mo ALD using molybdenum hexacarbonyl $[Mo(CO)_6]$ as the precursor.

Films of metallic Mo were produced by the atomic hydrogen (at-H) reduction of ALD MoO_3 films obtained from $Mo(CO)_6$ and ozone (O_3). The reduction of MoO_3 with molecular hydrogen (H_2) at temperatures beyond the BEOL limit is well-known and commercially utilized [6]. This work investigated the feasibility of bringing the temperature well below the BEOL limit by replacing H_2 with at-H.

First, a reliable ALD process for MoO_3 growth was developed by determining an appropriate ALD cycle (Fig. 1) and process temperature (Fig. 2). According to spectroscopic ellipsometry, the resulting films showed a 2-3% film thickness non-uniformity across the 100 mm wafer (Fig. 3). X-ray photoelectron spectroscopy (XPS) confirmed the MoO_3 stoichiometry (Fig. 4a). The as-deposited MoO_3 films were then exposed in situ to a steady supply of (hot wire generated) at-H for 30 min at 150 °C. A shift in the peak position of the Mo3d doublet from 234/237 eV to 228/231 eV showed a transition from an oxidized to a metallic state of Mo (Fig. 4b). The existence of satellite peaks corresponding to Mo in a non-zero oxidation state indicated the need to increase the reduction temperature. Another sample was reduced for 30 min at 350 °C, significantly lowering the satellite peak intensity (Fig. 4c). Performing angle-resolved XPS measurements on the samples revealed a gradual increase of the metallic Mo phase at the surface compared to that in the bulk (Fig. 5).

Implementing super cycles by introducing an at-H pulse during each ALD cycle resulted in highly oxidized films, indicating the importance of applying a final at-H reduction step to obtain metallic Mo films. Similarly, an ALD cycle that excluded O_3 oxidation but solely included at-H reduction resulted in a non-self-limiting deposition of Mo films with significant shares of carbon (15-25 at%) and oxygen (10-20 at%). Based on these findings, we conclude that the formation of pure Mo from $Mo(CO)_6$ below the BEOL limit requires an oxidation route to remove carbon efficiently; the intermediately formed MoO_3 can then be reduced in at-H to metallic Mo.

11:15am AF2-WeM-14 Growth of Metallic Ru Film by Oxidant-Free Atomic Layer Deposition Below 100 °C, *Kyeongmin Min, H. Lee,* Incheon National University, Republic of Korea*; C. Nguyen,* Incheon National University, Viet Nam

Ru is one of the very well-known metals in atomic layer deposition (ALD) researches because of its potential applications in the interconnect technology of Si devices. The main drawback of Ru ALD processes reported so far, however, is the oxidant counter reactants, such as O_2, O_3, and H_2O. In ALD, most of the noble metals, including Pt, Ir, and Ru, could be deposited by using oxygen counter reactant through their combustion reactions, so the oxidation of substrate underneath of the noble metal films could not be avoidable. The oxidation of substrate increases contact resistance of Ru, so it is not desirable in the interconnect applications. In this study, we deposited a high purity Ru film through thermal H_2 plasma ALD at low deposition temperature below 100 °C without any oxidant counter reactants. The thermal plasma was generated by exposing the H_2 counter reactant gas to a filament with high temperature over 1600 °C. By the high thermal energy of the filament, the H_2 gas molecules are dissociated into high energy radicals, and the radicals play an important role as a reactant in the thermal plasma ALD process. A high purity and conformal Ru film was obtained, and the resistivity of Ru film was 25 μΩcm. The metallic Ru films could be formed even at the low temperature, 80 °C. The resistivities of Ru films were X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) showed very low impurity levels below 5% in carbon and oxygen spectra. From the results of this work, we believe that the thermal plasma ALD could be widely applied to many applications which have critical issues in the oxidation of bottom layer and increase of contact resistance.

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11:30am AF2-WeM-15 Unveiling the Effect of the Starting Precursor on Ge₂Sb₂Te₅ Atomic Layer Deposition, *Jyoti Sinha,* KU Leuven, IMEC Belgium*; J. Innocent, A. Illiberi, M. Givens,* ASM, Belgium*; L. Nyns, A. Delabie,* IMEC Belgium

Chalcogenide materials like $Ge_2Sb_2Te_5$ (GST) are widely studied for application in memory devices [1]. To address the material needs resulting from the architectural device challenges within storage class memory (SCM), atomic layer deposition (ALD) has emerged as a prominent solution. Pore et al. have demonstrated a low temperature ALD process for GST using $GeCl_2.C_4H_8O_2$, $SbCl_3$, and $Te[(CH_3)_3Si]_2$ as precursors [2]. This process comprises the two binary ALD processes of GeTe and Sb_2Te_3 in a specific ratio to target the desired $Ge_2Sb_2Te_5$ composition, using either $GeCl_2.C_4H_8O_2$ or $SbCl_3$ as the first precursor pulse. This first pulse could affect the final film composition, and as such affect device performance.

In this work, we therefore study how the starting precursor influences the GST growth behavior and layer composition when deposited on SiO_2. The deposition on the SiO_2 substrate is initially Ge-rich, irrespective of the starting precursor, and gradually evolves to the desired 2:2:5 Ge:Sb:Te ratio when the thickness increases. The ideal composition is reached after 36 cycles. The interfacial Ge content is slightly higher when the GST ALD process starts with a $GeCl_2.C_4H_8O_2$ reaction as compared to starting with a $SbCl_3$ reaction, according to X-ray Fluorescence (XRF).

The chemical reactions at the GST/SiO_2 interface are investigated more thoroughly through chemisorption experiments, where we apply a single precursor reaction and measure the surface concentration of either Ge, Te or Sb ex-situ by means of total reflection XRF (TXRF). The results indicate that $GeCl_2.C_4H_8O_2$ has a higher reactivity towards SiO_2 than $SbCl_3$, as the concentration of Ge is ~4 times higher than the concentration of Sb. Almost no Te was observed after a single $Te[(CH_3)_3Si]_2$ reaction, indicating very low reactivity. We also investigate the subsequent Ge, Te, and Sb precursor reactions after a first Sb, Te, or Ge precursor reaction on SiO_2 and analyze the results assuming that only ligand exchange reactions take place, according to the model in [3]. Based on the concentration of Ge, Te, and Sb, we propose that Ge could react with two surface hydroxyl groups on the SiO_2 surface. On the other hand, due to the lower reactivity of $SbCl_3$, we propose that there are still unreacted surface hydroxyl groups after the $SbCl_3$ reaction that can react with $GeCl_2.C_4H_8O_2$ during the next pulse. This model leads to an overall Ge-rich GST at the interface, irrespective of the starting precursor.

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11:45am AF2-WeM-16 Atomic Layer Deposition Equipment Vendors Market and Technology, *Taguhi Yeghoyan,* Yole Group, France

From many years, Atomic Layer Deposition (ALD) and Atomic Layer Etch (ALE) have enabled subsequent generations of logic and memory. In 2024, ALD and ALE is again indispensable to drive innovation across patterning approaches, architecture change for transistor (FinFET to Gate All Around) and memory (DRAM to 3D DRAM or 3D NAND layer increase) as well as improve the performance of specialty devices (CMOS Image Sensors, BCD Power Si devices, SiC devices, integrated RF devices) .

These advancements are enabled by ALD and ALE equipment vendors who provide complete solutions that consider precursors, substrates, and processing problematics. Their efforts generate a collective 2023 market size of 3.3USDB for thermal and plasma equipment, representing 13% of the total deposition Wafer Fab Equipment (WFE) market. With further ALD and ALE needs, we expect this number to grow to 4.9USDB in 2029 with a 4.9% CAGR23-29, outperforming the overall WFE.

Via the market research, we aim to lay out the landscape of the industrial ALD and ALE equipment providers worldwide and highlight their innovative solutions proposed, which lead to specific market shares. Moreover, we draw a market forecast driven by mentioned CapEx hungry devices. Finally, we breakdown the market size to different device applications, wafer size, thermal and plasma ALD technologies.

Atomic Layer Etching
Room Hall 3F - Session ALE1-WeM

Plasma and Energy-Enhanced ALE
Moderator: Christophe Vallée, University of Albany

8:00am ALE1-WeM-1 Anisotropic and Isotropic Plasma-Enhanced Atomic Layer Etching Processes for Metals and Dielectric Materials for Semiconductor Devices, *Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea **INVITED**

The critical dimensions of semiconductor devices are continuously shrinking with 3D device structure and are approaching to nanometer scale. The demand for dimension control in angstrom level is drastically increasing also in etching processes. In this talk, various plasma-enhanced ALE (PEALE) processes are discussed for anisotropic and isotropic patterning of metals and dielectric materials including molybdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, aluminum oxide, hafnium oxide, zirconium oxides, silicon oxide, and silicon nitride. [1-10] Typical ALE processes consist of surface modification step and removal step. Various surface modification schemes were applied including fluorocarbon deposition on surface, surface fluorination, surface chlorination, surface oxidation with radicals generated with plasmas. For the removal or etching step, the modified layers were removed by ion-bombardment, heating, ligand exchange, ligand volatilization, or halogenation. The characteristics of reaction kinetics, surface roughness, surface residue in the plasma-enhanced ALE processes will be also discussed.

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8:30am ALE1-WeM-3 Plasma Atomic Layer Etching of Titanium Nitride with Surface Fluorination or Chlorination and Ar Ion Bombardment, *Heeju Ha,* H. Lee, M. Jeon, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea

Plasma atomic layer etching (ALE) processes were developed for titanium nitride (TiN) with surface fluorination or chlorination in the modification step and ion bombardment in the removal step. In the modification step, the TiN surface was fluorinated using NF_3 plasma to form Ti-F bonds or chlorinated using BCl_3 plasma to form Ti-Cl bonds. The fluorinated or chlorinated layers were removed by ion bombardment using Ar plasma. The etch per cycle (EPC) of TiN was investigated depending on ion energy and etching time. The ALE window of constant EPC of TiN was confirmed in the energy range of 25 – 80 V for fluorination and 70 – 80 V for chlorination. The EPC of TiN was determined to be 1.5 nm/cycle in fluorination and 3.8 nm/cycle in chlorination in the ALE window region. The EPC of TiN increased with increasing Ar plasma time and exhibits self-limiting properties at 180 seconds for both fluorination and chlorination. The strong Ti-F peak was observed about 13% on the surface after ALE process with fluorination, but small Ti-Cl peaks were observed below 1% after ALE process with chlorination. The Root-mean-square (RMS) roughness of the TiN surface after ALE was measured at 0.24 nm for fluorination and 0.29 nm for chlorination, which is lower than before etching.

8:45am ALE1-WeM-4 Isotropic Plasma Atomic Layer Etching of Nickel Aluminide Binary Intermetallic Using a Super-Cycle Sequence Based on Hhfac and Al(CH₃)₃, *Ali Mohamed Ali,* IMEC Belgium*; G. Krieger,* TU / Eindhoven, Netherlands*; J. Soulié, C. Pashartis,* IMEC Belgium*; C. Detavernier,* Ghent University, Belgium*; H. C. M. Knoops, E. Kessels,* TU / Eindhoven, Netherlands*; S. De-Gendt, F. Lazzarino, S. Kundu, J. de Marneffe,* IMEC Belgium

Nickel aluminides have attracted tremendous research attention as a potential alternative material for barrier-less interconnects and EUV mask absorber applications due to its lower resistivity than other elemental metals and higher printing resolution, respectively.[1,2] However, down-scaling these binary intermetallics brings emerging challenges in developing etch methods due to the high chemical inertness and low gas-phase volatility of Ni compounds. In addition, preserving the concentration of each element in the alloy during the etching process is essential to be useable at the nanoscale. In this work, we report a new and promising approach towards the atomic layer etching (ALE) of stoichiometric NiAl and Ni_3Al. A super-cycle ALE process has been developed, in which each sub-cycle enables the removal of the Al-rich and Ni-rich phases, respectively. Fluorine-containing plasma and trimethyl-aluminum (TMA) precursors have been utilized to etch Al in the first phase. Whereas, in the second phase, the etching of Ni has been achieved using a nitrogen-containing plasma, probably forming Ni nitride and then chelation by hexafluoro-acetylacetone (Hhfac) precursor. A fundamental ALE study on each individual ALE process has been performed on pure Ni and pure Al films to evaluate the etching efficiency and selectivity of each element versus the other. *In-situ* spectroscopic ellipsometry measurements were employed to elucidate the self-limiting nature of the ALE sequence on the pure metal film and thickness change during alloy etching. The saturation behavior for each precursor on the compatible pure metal films has been observed. X-ray reflectivity measurements were carried out to confirm the etch rates on Ni-aluminide films. The etch rates were varied from 0.5 ± 0.10 Å/super-cycle at 250 ˚C to 3.3 ± 0.23 Å/super-cycle at 350 ˚C. Furthermore, atomic force microscopy analysis shows that thin Ni aluminide films remained smooth during initial etching and might introduce a little roughness when the etch cycles progressed. The results obtained from x-ray photoelectron spectroscopy confirmed that, at the optimized super-cycle ALE process, the etched Ni aluminide films still preserve the same concentration of each element in the alloy. The developed ALE process enabled the etching of nickel aluminide alloys and created a paradigm for future studies on alternative etching of binary intermetallics.

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[2] Luong, Vu, et.al.“*Ni-Al alloys as alternative EUV mask absorber.*”Applied Sciences 8.4(2018):521.

9:00am ALE1-WeM-5 Surface Effects in Quasi-ALE of Si: A Correlation with Ar⁺ Ion Energy, *O. Danielsson,* Lund University, Sweden*; A. Karimi, Y. Ilarionova, M. Asif,* AlixLabs AB, Sweden*; S. Khan,* Danish Fundamental Metrology Institute, Denmark*; Ivan Maximov,* Lund University, Sweden

Atomic Layer Etching (ALE) is a self-limiting process used in nanofabrication that allows for precise material removal on the atomic scale by a cyclic

nature introducing reactive gas adsorption and removal of surface atoms by a low-energy ion bombardment. In practical realisation of ALE, e.g. using commercially available RIE tools, the ion energy in plasma may exceed the sputtering threshold, typically 20-40 eV. It will result in a quasi-ALE (Q-ALE) regime where the process steps are not self-limiting, but still highly accurate and of lower damage compared to RIE. Direct measurements of the ion energy in Q-ALE are thus instumental for studies of both the etching process and surface damage effects.

For Si etching experiments, we have used a commercial Inductively Coupled Plasma RIE Takachi™ tool from Plasma-Therm LLC, USA. The tool operates in a Cl_2-molecular activation regime using Ar RF-plasma to desorb the etch reaction products in the etch step. Unpatterned silicon-on-insulator (SOI) 10x10 mm^2 samples with a 50 nm thick top Si layer were used for the etching experiments and characterised by spectroscopic ellipsometry and AFM. Typically, the Q-ALE operated in a 25 cycle mode, sufficient to measure the Si thickness difference by ellipsometry using a 4-layer model. A Retarding Field Energy Analyzer (RFEA) from Impedance LLC, Ireland, was installed to measure the Ar^+ ion energy and ion current densities at different Q-ALE conditions, such as RF-power and pressure. The surface effects of the etched SOI samples are characterised by AFM, SEM and Kelvin Probe Force Microscopy (KPFM).

In this work we present the actual data of Ar^+ ion energy distribution and the ion current densities at the sample level in the commercial Takachi™ RIE tool operating in Q-ALE mode. In order to reach a low ion energy regime, we used RF-power in the range of 3-16 W, that corresponds to the bias voltages of 10-120 V. In this voltage range the ion energy peak shifts from ≈50 to 147 eV, respectively, with an increase in the RF-power. The calculated Ar^+ ion flux from the measured ion currents is about 3×10^{13} – 2×10^{14} ion cm^{-2} s^{-1} that fits well with the published data. Etch per cycle (EPC) was measured in both sputtering (no Cl_2) and ALE-regime at different bias set-points (RF-power). A clear EPC plateau for the ALE regime was observed at biases of 20-40 V that corresponds to the peak Ar^+ ion energy of 50-70 eV. The AFM and high-resolution SEM data demonstrated a decreased surface roughness of etched Si in the plateau region indicating a low surface damage. More details to be presented.

9:15am **ALE1-WeM-6 Atomic Layer Etching Study of Polycrystalline, Epitaxial and Doped ZnO Films Using** *in Situ* **Spectroscopic Ellipsometry**, *T. McNealy-James, N. Berriel, B. Butkus, T. Currie, T. Jurca,* **Parag Banerjee**, University of Central Florida

Atomic layer etching (ALE) offers sub-nm level control over film removal, with two distinct categories: ion-driven anisotropic etching and thermal isotropic etching. Both options present a promising solution to address patterning challenges in device manufacturing. These mechanisms become particularly important when the extended atomic structure of films such as crystal facets, grain boundaries, and dopants are taken into consideration.

In this work, we study the ALE of a model film - zinc oxide (ZnO), with particular emphasis on observing the role of crystallinity and doping in determining film etch rates. We employ *in situ* spectroscopic ellipsometry as our tool of choice and comprehensively map the etch rate as a function of temperature and co-reactant pulse times. The resulting 3D contour plot of etch rate *vs.* temperature and time depicts the process parameter window. Importantly, the plot is visually appealing and can yield insightful information pertaining to ALE processes, in general.

The ALE chemistry[1] employed to etch ZnO consists of alternate pulses of acetylacetone and O_2 plasma while the temperature is varied from 100 ^{o}C to 300 ^{o}C. The etch rates of single crystalline (*e.g.*, c-axis oriented) films are compared with polycrystalline ZnO. The effect of dopants, such as Al^{3+} and Ti^{4+}, on the etch rates of ZnO films are explored. The impact of ALE chemistry in determining etch rates in films with extended atomic structure such as crystal facets, grain boundaries and dopants are discussed with implications to future device manufacturing.

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9:30am **ALE1-WeM-7 Atomic Layer Etching of Diamond for Epitaxy Preparation**, *Julian Michaels,* University of Illinois at Urbana-Champaign; *N. Delegan,* Argonne National Laboratory, USA; *Y. Tsaturyan,* University of Chicago; *J. Renzas,* Oxford Instruments Plasma Technology; *D. Awschalom,* University of Chicago; *J. Eden,* University of Illinois at Urbana-Champaign, USA; *F. Heremans,* Argonne National Laboratory, USA

Renowned for its exceptional hardness and chemical impermeability, diamond is a wide bandgap semiconductor material with promising applications in optoelectronics, quantum optics, and beyond. Despite its desirable properties, the inherent manufacturing and fabrication challenges associated with monocrystalline diamond make it difficult to smooth, leading to lossy devices in its various applications. Moreover, existing methods for surface smoothing are often costly and time intensive.

In this context, atomic layer etching (ALE) emerges as a potentially viable solution for smoothing diamond surfaces. ALE is a cyclical process that precisely defines nanostructures by removing individual atomic layers. Recently, bias-pulsed ALE (BP-ALE), which is an augmented ALE process wherein reagent gases are not purged between steps, was shown to drastically smooth the surface of 4H-SiC substrates.

Here, we present a novel BP-ALE recipe tailored for diamond substrates. This innovative approach not only achieves precise etching of diamond but also facilitates rapid surface smoothing compared to existing conventional methods. To evaluate the efficacy of BP-ALE, diamond films were grown on etched surfaces, conventionally smoothed substrates, and commercially purchased substrates. Our findings indicate that BP-ALE not only expedites surface smoothing but also yields growth-ready surfaces suitable for subsequent diamond growth.

In summary, our study underscores the potential of BP-ALE as a cost-effective and efficient method for smoothing diamond surfaces, thereby enhancing their suitability for various optoelectronic and quantum optical applications.

Atomic Layer Etching
Room Hall 3F - Session ALE2-WeM

Selectivity, Metrology and Diagnostics in ALE
Moderators: Adrie Mackus, Eindhoven University, Netherlands, **Gregory N. Parsons**, North Carolina State University

10:45am **ALE2-WeM-12 Interest and Potential of Atomic Layer Etching for Selective Deposition**, *T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France; *M. Jaffal,* University Grenoble Alpes, CNRS, LTM, France; *R. Gassilloud,* CEA/LETI-University Grenoble Alpes, France; *N. Possème,* ST Microelectronics, France; *C. Vallée,* University of Albany; **Marceline Bonvalot**, University Grenoble Alpes, CNRS, LTM, France **INVITED**

Selective deposition processes have attracted increased research interest in recent years due to their ability to precisely deposit thin films on specific substrate areas (for area-selective deposition) or on surfaces with specific orientations (for topographical selective deposition). These processes require a growth kinetic controlled by precursor/surface interactions with an atomic-scale precision, which usually relies on Atomic Layer Deposition (ALD) techniques with or without plasma assistance (PEALD).

Several approaches have been proposed for selective deposition involving surface inhibition treatments with specific chemical agents (such as self-assembled molecules, small molecule inhibitors, plasma treatment) that increase the nucleation delay during subsequent ALD growth. However, the inhibition behavior eventually deteriorates after exposure to a few ALD cycles, necessitating the removal of nuclei formed on non-growth surfaces and the systematic regeneration of the inhibitor.

Another pathway for selective deposition is to combine ALD with Atomic Layer Etching (ALE). ALE involves self-limiting reactions that occur in a cyclic manner and consisting in a surface modification step followed by a removal step of the previously modified layer. Such a process results in the controlled and selective removal of a thin material layer.

In this presentation, we will focus on the interest and capabilities of ALE or quasi-ALE process for selective deposition. Based on several application examples such as liner deposition, we will highlight potential and related issues by coupling ALD and ALE for topographical selective deposition (growth and etch per cycle, selectivity with respect to the underneath layer, cross contamination...). We will also discuss about tools strategy to combine both ALD and ALE processes.

11:15am ALE2-WeM-14 Insight into SF$_6$/H$_2$ Plasma Mixtures to Expand the Capabilities of ALE, *Guillaume Krieger, S. Peeters, B. Vonken, N. Chittock, A. Mackus, E. Kessels,* Eindhoven University of Technology, The Netherlands; *H. Knoops,* Oxford Instruments Plasma Technology, The Netherlands

The continuous downscaling of nanoelectronics combined with the ever-increasing diversity in materials and 3D geometries calls for highly precise and selective etching processes. Therefore the atomic layer etching (ALE) community must continue to develop a diverse toolbox of processes to enable both anisotropic and isotropic etching of the library of materials required in IC fabrication. Within this toolbox, recent works involving SF$_6$:H$_2$ plasma mixtures have demonstrated promising results for the etching of Si- and Ti-based materials[1,2], with improved selectivity. However the etching mechanism is not yet well understood. Notably, the plasma species responsible for the onset of etching at a specific SF$_6$:H$_2$ ratio need to be identified.

Here, we present our first results from quadrupole mass spectroscopy (QMS) and optical emission spectroscopy (OES) measurements on SF$_6$:H$_2$ plasma mixtures. The plasma power, pressure and SF$_6$:H$_2$ ratio have been varied to observe their respective influence on the plasma composition. OES measurements show a high F radical emission intensity for SF$_6$ rich plasma mixtures. QMS measurements reveal a maximum intensity of the m/z=20 signal, which could be related to the presence of HF, for a ratio of SF$_6$/(SF$_6$+H$_2$) between 0.24 and 0.3. At this same ratio of plasma mixture, the signal of the m/z=34 mass (*i.e* H$_2$S) drops drastically while the m/z=89 signal (*i.e* SF$_3^+$ acting as a fingerprint for SF$_6$) starts to increase. Interestingly, under the same conditions, this specific range of gas ratios coincides with the etching onset of TaN at SF$_6$/(SF$_6$+H$_2$)≈0.25. Furthermore, when an oxygen gas exposure step is added in the process, the oxidized TaO$_x$N$_y$ top-layer can be etched at a smaller SF$_6$/(SF$_6$+H$_2$) ratio≈0.2, equivalent to the etching onset of SiO$_2$. These results show similarities to the selective ALE process reported by Hossain *et al.*[1] between TiN and TiO$_2$, occurring at a SF$_6$/(SF$_6$+H$_2$)≈0.17, close to the ratio we report for TaN. By identifying the main trends in the plasma species present in the SF$_6$/H$_2$ plasma and comparing these observations to the ALE process window, we aim to improve the understanding of the underlying etching mechanisms. A greater knowledge of this process will help to extend this ALE chemistry to a wider range of materials.

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1. Hossain, A. A. *et al., JVST A* **41**, 062601 (2023).
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11:30am ALE2-WeM-15 Retarding-Field Energy Analyzer as a Tool to Find the Process Window for Plasma-Assisted Atomic Layer Etching and Quasi-Atomic Layer Etching, *Yoana Ilarionova, R. Jam, I. Sharma, O. Danielson, S. Ju, A. Muhammad, D. Suyatin, A. Karimi, J. Sundqvist,* AlixLabs AB, Sweden

As the fabrication of chips gets more demanding, atomic layer etching (ALE) provides a controlled way of etching without the surface damage typically associated with reactive-ion etching (RIE). ALE features 2 main steps – surface modification and etch. If inert-ion plasma is chosen to etch, ion energy makes the difference between ALE and physical sputtering. This is why the ion energy distribution function (IEDF) is a very important property when designing plasma-assisted ALE processes.

In this study, we used retarding-field energy analyzer (RFEA) System from Impedans Ltd for IEDF measurements. This enabled us to effectively find and tune the ALE process windows for Si and III-V materials. The experiments were done with Ar plasma in a few standard etch chambers for inductively-coupled plasma reactive ion etching (ICP-RIE) from different vendors. We examined how different process parameters and their interplay influence the IEDF. This is very important for understanding the right combination of process parameters for ALE and the limitations of quasi-ALE processes that can be achieved with this equipment. This also guides in finding the right hardware modifications for improving the ALE processes and their stability in conventional equipment readily available in research labs and semiconductor fabs. This is also valuable for designing dedicated hardware for ALE processes, especially for industry.

Emerging Materials
Room Hall 3E - Session EM-WeM

Molecular Layer Deposition of Organic Materials and Organic-Inorganic Hybrid Materials

Moderators: Christophe Detavernier, Ghent University, Belgium, **Paul Poodt**, SparkNano

8:00am EM-WeM-1 Resolving Composition and Crystal Structure of Fundamentally Novel MOF-Like Fe-Terephthalate Thin Films, *Topias Jussila, A. Philip,* Aalto University, Finland; *V. Rubio-Giménez,* Katholieke Universiteit Leuven, Belgium; *K. Eklund,* Aalto University, Finland; *S. Vasala,* ESRF - The European Synchrotron, France; *A. J. Karttunen,* Aalto University, Finland; *R. Ameloot,* Katholieke Universiteit Leuven, Belgium; *M. Karppinen,* Aalto University, Finland

Crystalline metal-organic framework (MOF) materials are anticipated for various applications due to their diverse material properties, yet they lack industry-feasible fabrication methods.[1] The atomic/molecular layer deposition (ALD/MLD) technique is in many aspects superior to the traditional solvent-based thin-film fabrication techniques of hybrid metal-organic materials, as it provides solvent-free thin films with precise thickness control and direct device integration. Most excitingly, the ALD/MLD enables the in-situ growth of even fundamentally novel MOF-like materials.[2] Iron-terephthalate (Fe-BDC) is one of the most appealing MOF materials and thus widely studied in bulk form owing to its attractive potential applications in photocatalysis, biomedicine, and beyond.[3]

Here we obtain through ALD/MLD in-situ crystalline, air-stable Fe-BDC thin films different from the Fe-BDC MOFs prepared in bulk form.[4] These thin films are characterized with a combination of advanced experimental and computational methods such as synchrotron grazing-incidence X-ray diffraction (GIXRD) and resonant inelastic X-ray scattering (RIXS) to disclose their unique chemical and structural features. The investigations reveal the existence of both Fe(III) and Fe(II) in the films and, excitingly, converge towards a novel crystalline Fe(III)-BDC phase with space group *C*2/*c* (Figure 1), and a previously unknown amorphous Fe(II)-BDC phase. Resolving the structure of a thin film material can be exceedingly demanding for materials with no bulk counterparts to compare with as traditional methods such as Rietveld refinement cannot be realized for thin films; this work provides a valuable example how the novel structures can be nevertheless determined.

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8:15am EM-WeM-2 Molecular Layer Deposition of Metal Organophosphonate Thin Films, *Aditya Chalishazar, A. Dhara, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Molecular layer deposition (MLD) can be used to incorporate organic moieties in thin films, resulting in hybrid -----organic--inorganic films [1,2]. Hybrid films are uniquely interesting due to the combination of the desirable properties of the organic and inorganic components [3]. However, MLD films often suffer from low chemical and hydrolytic stability, limiting their commercial success [4,5].

Phosphorus-containing hybrid materials (organophosphates) can be promising alternatives to conventional Si-based hybrid materials such as silicones. The stability of the P–O–M and P–C bonds [bond dissociation energy: P–C: 513 kJ/mol vs. Si–C: 435 kJ/mol] results in thermally and chemically stable hybrid materials. Among others, metal phosphonates are an interesting class of organophosphorus materials, with applications spanning ion exchange, proton conductors, anti-fouling coatings, catalysts and membranes. However, their deposition by MLD has yet to be explored.

We report the synthesis of novel hybrid aluminium phosphonate layers developed with MLD using trimethylaluminium (TMA) as the metal source and a novel phosphonate ester, dimethoxyphenylphosphonate (DMPP), as the phosphorus source. The growth of these films has been explored using two different dosing sequences (Figure 1) and studied with *in-situ* ellipsometry. At 250 °C, the three-step sequence yields a growth per cycle (GPC) of 0.4 Å/cycle, while the GPC of the four-step sequence was 0.8 Å/cycle. Both dosing schemes are observed to saturate (Figure 2a), with ALD-like growth above temperatures of 200 °C. The deposited films are characterised using FTIR (Figure 2b) and XPS, which establish the incorporation of the phenyl phosphonate components into the MLD film.

In view of applications, the temperature-dependent ionic conductivity of these films was explored from 100 to 400 °C, with the conductivity improving in a humidified environment (Figure 3a). The thermal (Figure 3b) and water (Figure 3c) stability of the films has also been studied, with the layers showing superior thermal stability (> 500 °C in air) and complete water stability after immersion for one hour. Finally, to verify the generality of this deposition approach, the organic group on the phosphonate backbone was varied, and the subsequent impact on the functional properties of the films was studied.

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[2]   *Advanced   Materials   Interfaces*,   **2022**,   *9*,   2200210
[3]   *Chemistry   of   Materials*,   **2001**,   *13*,   3283
[4]   *RSC   Advances*,   **2015**,   *5*,   29947
[5] *Dalton Transactions*, **2016**, *45*, 1176

8:30am **EM-WeM-3 Europium-Organic Luminescent Thin Films for Bioimiging Applications**, *Amr Ghazy,* Aalto University, Finland*; J. Ylönen, N. Subramaniyam,* Xfold imaging oy, Finland*; M. Karppinen,* Aalto University, Finland

The Förster resonance energy transfer (FRET) technique is currently employed in the biological detection of several viruses. In FRET, two chromophores are used, a donor and an acceptor [1]. Thanks to their intriguing luminescence properties, such as long lifetimes, and color pure sharp emissions, Ln^{3+} compounds are prime candidates as donor chromophores for FRET [2].

In FRET, the efficiency of energy transfer depends mainly on the distance between the donor and the acceptor chromophores. While the transfer becomes significantly weak when the distance is larger than 5 nm, no energy transfer occurs at 10 nm [3]. This leads to an issue when considering the typical Ln^{3+} materials in colloidal solutions. As being suspended in a mobile phase the distance between the Ln^{3+} donors and acceptors varies significantly. One solution is the use of a solid state immobile phase for the Ln^{3+} donors.

Atomic/molecular layer deposition has been recently utilized in developing Ln^{3+} photoluminescent thin films. However, these films usually require UV light as an excitation source, which can be detrimental to biological samples [4]. In our work, we developed a new process based on Eu^{3+} that can be excited by the less damaging visible light.

Thin films of Eu-HQA were grown from Eu(thd)3 as a metal precursor and 2-hydroxyquinoline-4-carboxylic acid (HQA) as an organic precursor. The process was developed at 210 °C, and yielded uniform films with a GPC of ~ 7.3 Å/cycle. The films showed a wide excitation wavelength range stretching between 185 nm in the UV region and up to 425nm in the visible light (fig. S1). These films can be deposited on various substrates, including glass and polymers, but most interestingly depositing on a plasmonic surface with complex structure (X-fold) is also possible. The plasmonic structure resonates with the excitation wavelength leading to a 20-fold increase in the emission strength of the films compared to the emission from similar film grown on plain Si substrates (fig. S2) .

Eu-HQA films on plasmonic surface can be used in combination with a FRET acceptor chromophore Alexa Flour 647 (AF) to show FRET emission. The films show the Eu^{3+} typical emission at 615 nm. Upon the addition of AF, the emission is transferred to AF, which emits light at 650 nm. This can be seen by a decrease in the intensity emission of Eu^{3+} at 615 nm, and an increase in the emission at 650 nm (fig S2).

References

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[4] A. Ghazy et. al, Chem. Mater., 2023, 35, 5711 —6178.

8:45am **EM-WeM-4 ALD Young Investigator Award Finalist Talk: Inverted Living Molecular Layer Deposition: An Empowering Technique for Biomedical Applications**, *Karina Ashurbekova, M. Knez,* CIC nanoGUNE BRTA, Spain

Polymeric molecules are born in an initiation process, they grow by a propagation process, and finally they 'die' in a termination process.

-SZWARC, M. 'Living' Polymers.*Nature* (1956).

This study shows an inverted living molecular layer deposition technique which facilitates controlled polymer growth with desired architecture, functional moieties, and adjustable properties.

We report on the first vapor phase growth of polyoxazolines (POx) through a living cationic ring-opening polymerization (CROP) mechanism. The two-step process includes a pulsed supply of a vaporized initiator (P-Toluenesulfonyl chloride) to a reactor space, which functionalizes a substrate by adsorbing as a molecular layer. This is followed by the chain propagation after the monomer is supplied and interacts with the layer of the chemisorbed initiator. We used three substituted oxazolines as monomers: 2-methyl-2-oxazoline, 2-phenyl-2-oxazoline and 2-isopropenyl-2-oxazoline. After exposing the substrate to the monomer vapors for several seconds the chamber is purged, and another portion of the vaporized monomer is introduced. With each monomer pulse, the thickness of the polymer layer increases until the monomer is consumed, which makes it possible to control the final thickness of the coating with the dose and the number of monomer feed cycles. The supply of water vapor to the reactor causes the growth to terminate. The living nature of the polymerization has been confirmed by *in situ* QCM studies. The composition, morphology, and thermal stability of the POxs have been evaluated by ATR-FTIR and XPS spectroscopies and thermogravimetric analysis (TGA).Although in this presentation we show only the growth of POx homopolymers, copolymerization via sequential monomer addition is also possible. The main advantages of this approach include absence of multicomponent solution-based impurities, thickness control, conformality and strong adhesion of the films to most substrates.

Extensive biological studies on biocompatibility, immunotoxicity, and control of protein and cell adhesion have provided positive results, underscoring the relevance of POx in biomedicine. (1) The demonstrated approach serves only as proof of principle and offers plenty of space for further investigation and adaptation of materials for specific applications. Thus, the present development is a starting point for a new way of surface functionalization with functional polymeric materials.

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9:00am **EM-WeM-5 Hybrid Multilayer EUV Photoresist with Vertical Molecular Wire Structure**, *Myung Mo Sung,* Hanyang University, Republic of Korea   **INVITED**

Basic requirements for good patterns using extreme ultraviolet lithography (EUVL) are sensitivity, resolution, line edge roughness (LER), outgassing, etch resistance, defect density, and reproducibility. Among them, it has been proved that resolution, LER, and sensitivity (RLS) are interdependent with each other. The trade-off between RLS pose a critical challenge in the race towards device downscaling to 1 nm node. LER is the most important consideration to determine the manner in which EUVL will be employed. Recently, we develop a new EUV dry resist with organic-inorganic hybrid multilayer structures vertically tailored with several functional layers by using molecular layer deposition. Additionally, each layer includes a self-assembled organic monolayer to generate a vertical molecular wire structure. The hybrid multilayer resist shows high EUV sensitivity from the high EUV absorbing and reactive layers there. Furthermore, the vertical molecular wire structure of the hybrid resist generates exceptionally low LER.

9:30am **EM-WeM-7 Chemical Transformations Mediated by Low-Energy Electrons within Vapor Phase Synthesized Al-based Hybrid Thin Films for Advanced Resist Applications: An In-Situ Investigation**, *Dan Le,* T. Chu, University of Texas at Dallas*; W. Lee,* Stony Brook University*; N. Tiwale,* Brookhaven National Laboratory*; J. Veyan, J. Kim, D. Kim, M. Lee,* University of Texas at Dallas*; C. Nam,* Stony Brook University/Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas

The adoption of higher (>0.55) or hyper (≥0.75) numerical aperture (NA) in EUV lithography is crucial for sustaining extreme downscaling of device features (<1-nm node), necessitating the adoption of novel resist platforms to meet the stringent demands.[1] Key targets of such EUV resists include achieving <20 nm thickness, homogeneity, mechanical and chemical

stability, and high etch resistance.[1,2] However, attaining these essential targets using conventional spin-coating-based resists presents challenges. In this context, vapor-phase synthesized inorganic-organic hybrid dry resists offer advantages, in terms of ability to control resist thickness at the atomical scale and material homogeneity; and incorporating metal elements to enhance sensitivity, mechanical stability, as well as etch resistance.

Herein, we present a molecular atomic layer deposited inorganic-organic hybrid thin film system, consisting of TMA and HQ, for dry EUV resist applications, where negative tone resist characteristics were observed. Such characteristics of hybrid materials are reproducible at various electron energies (Fig. 1a-1c). Through *in-situ* FTIR and *in-operando* RGA analyses (Fig. 1d-1e), we elucidate the chemical transformations induced by electrons with energy as low as 80 eV, wherein the Al-based hybrid thin films underwent a dehydrogenation process and structural rearrangement, forming a crosslinked carbon network (Fig. 1f). Raman analysis further indicates that structural rearrangement of hybrid thin films leads to a formation of graphitic carbon domains (Fig. 1c).[3] Our study also reveals that the thickness degradation, upon exposure to the ambient condition, does not impede the patterning ability of the hybrid materials. The XPS and *in-operando* RGA spectra suggest that some of the additional C=O species formed during the aging period become volatile byproducts during electron exposures, thereby allowing the expected structural arrangement to proceed. Given the recent emergence of dry resists, the fundamental understanding of interactions between EUV photons/ primary and secondary electrons and resist materials is limited. Gaining insight into these chemical alterations as well as assessing hybrid material stability will undoubtedly contribute to the advancement of resist technology for future-generation lithography applications.

[1]IRDS International Roadmap for Devices and System – 2023 Update Lithography & Patterning

[2]H. Suh *et al., Proc.* SPIE **12498**, 1249803 (2023).

[3]S. Lee *et al., Dalton. Trans.* **50**, 9958 (2021).

9:45am **EM-WeM-8 Molecular Layer Deposition of Phosphorus Thin Films Using Bis-α-aminophosphine Chemistry**, *Justin Lomax, J. Bentley, P. Ragogna,* University of Western Ontario, Canada

Various organic substances like amides, ureas, terephthalates, and esters have been explored in molecular layer deposition (MLD), however the use of phosphorus-based precursors remains relatively unexplored.[1] One approach to synthesize P-containing polymer thin films, is to translate a solution phase process into a gas phase one. In this context, we have employed a primary phosphine, an imine and O_2/S_8 (Ch) to craft bis-α-aminophosphinechalcogenide materials.[2] Diazabutadiene (DAB) and primary phosphines (iBuPH$_2$ & CyPH$_2$) showed suitable precursor volatility for film deposition on primer functionalized SiOH surfaces. Depositions of films were carried out in a custom-built crossflow ALD reactor attached to a glovebox for air free handling (pulse/purge sequence: R-PH$_2$ 0.1 s/30 s; DAB 5 s/30 s; Ch 0.1 s/30 s). Additional surfaces of patterned Au/SiOH wafers were prepared to establish selectivity factors when using pre-functionalized surfaces. Small molecule synthesis, precursor volatility, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and Atomic Force Microscopy (AFM) techniques will be discussed.

(1) Meng, X. An Overview of Molecular Layer Deposition for Organic and Organic–Inorganic Hybrid Materials: Mechanisms, Growth Characteristics, and Promising Applications. *J. Mater. Chem. A***2017**, *5* (35), 18326–18378.

(2) Lamberink-Ilupeju, J.-W.; Willans, M. J.; Gilroy, J. B.; Noël, J. J.; Blacquiere, J. M.; Ragogna, P. J. Multicomponent Synthesis of Poly(α-Aminophosphine Chalcogenide)s and Subsequent Depolymerization. *Inorg. Chem.***2023**, *62* (37), 15104–15109.

ALD Applications
Room Hall 3D - Session AA1-WeA

More than Moore Applications
Moderators: **Benjamin Greenberg**, Naval Research Laboratory, **Sami Sneck**, Beneq

1:30pm AA1-WeA-1 ALD Solutions for Compound Semiconductor Devices, *Mikko Söderlund, A. Voznyi, T. Ivanova, A. Perros, P. Rabinzohn,* Beneq Oy, Finland **INVITED**
Among the wide bang gap (WBG) WBG semiconductors, SiC and GaN offer attractive performance over Silicon-based devices for the realization of high-voltage switches to be used in power converters and have been widely adopted for many applications.Tesla's adoption of SiC in 2017 for the onboard, or traction, inverters for its Model 3 was an early and major win. EV traction inverters typically range from about 35 kW to 100 kW for a small EV to about 400 kW for a large vehicle.On the other hand, AlGaN/GaN High-Electron-Mobility-Transistors (HEMTs) have allowed realization of low on-resistance and high-switching frequency transistors, enabling GaN-based power FETs rating 650 V with preferred normally-off device performance achieved using a p-GaN gate stack.

However, both SiC and GaN-based power transistors face challenges with defectivity of the semiconductor-dielectric interface, reducing the device electrical performance and especially on-resistance to less than ideal. In particular, low electron mobility at the SiO2/SiC interface due to carbon-related interface defects resulting from thermal oxidation remains the number one challenge for SiC devices and is associated with hysteresis of threshold voltage. Thus, a clear industry trend is to eliminate oxidation from the SiO2 formation process. The formation/deposition of highest-quality gate dielectric stacks (including SiO_2 and high-k) by atomic layer deposition (ALD) with the capability to control the dielectric/SiC interface by in-situ surface treatment and plasma enhanced atomic layer deposition (PEALD) Interfacial Layers (IL) are expected to play a significant role in the manufacturing of high performance SiC MOSFETs.

This paper presents an industrially proven three-step PEALD/thermal ALD cluster tool approach to engineer and perfect the semiconductor/dielectric interface quality and deposition of dielectric stack applicable to both GaN and SiC power devices. Characteristics of capacitance voltage (CV) and current density voltage (JV) for 4H-SiC MOS capacitors that utilize either ALD SiO_2 only, or ALD SiO_2 after plasma preclean (PP) or ALD SiO_2 with IL, are measured and presented. Overall, all devices demonstrate high-breakdown, low leakage current and negligible CV hysteresis indicating high-quality of ALD SiO_2 film and low-density of traps at the SiC/SiO_2 interface. In the best condition with PP/SiO2, nearly ideal SiC-SiO2 interface with hysteresis of less than 20 mV is achieved while demonstrating very low trapped charges. Improvement of p-GaN gate HEMT dynamic Rds on-resistance by ALD passivation layer will also be presented.

2:00pm AA1-WeA-3 Plasma Effects on the Epitaxial Growth of Aluminum Nitride Thin Films on (0001)4H-SiC by PE-ALD, *Bruno Galizia, P. Fiorenza, C. Bongiorno,* Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi (CNR-IMM), Italy*; B. Pécz, Z. Fogarassy,* Centre for Energy Research, Institute of Technical Physics and Materials Science, Hungary*; G. Greco, F. Giannazzo,* Consiglio Nazionale delle Ricerche - Istituto per la Microelettronica e Microsistemi (CNR-IMM), Italy*; F. Roccaforte,* Consiglio Nazionale delle Ricerche - Istituto per la Microelettronica (CNR-IMM), Italy*; R. Lo Nigro,* Consiglio Nazionale delle Ricerche - Istituto per la Microelettronica e Microsistemi (CNR-IMM), Italy
Aluminum Nitride (AlN) is considered a suitable candidate for the replacement of SiO_2 as gate dielectric in 4H-SiC based power MOSFETs because of its high permittivity constant (~9.1), large bandgap and good band-offset with 4H-SiC. Moreover, epitaxial growth and good interface quality could be favored by its low in-plane lattice mismatch with 4H-SiC (~0.9%) and because of their similar thermal expansion coefficients. Several deposition techniques such as molecular beam epitaxy, metal-organic chemical vapour deposition or physical vapour deposition have been used as AlN thin film synthesis technique, but they all suffer from high temperature processing.In this work, we investigated lower temperature PE-ALD processes, depositing AlN thin films on (0001)4H-SiC substrate at 300°C and we studied the effects of NH₃ plasma pulse time on crystalline quality, structural and electrical properties. Precursor nucleation and plasma effects have been monitored via *in-situ* ellipsometric spectroscopy half-cyle and end-cycle measurements and it has been observed that different AlN cristalline phases have been formed as a function of plasma time pulsing. In particular, the wurtzite AlN structure is always present at the interface with the 4H-SiC substrate, while upon increasing thickness a poly-crystalline wurtzite phase was obtained by short-pulse NH₃-plasma, whereas longer plasma exposure resulted in a mixture of wurtzite and zincblende defective phases. The different phase formation has been also related to electrical properties by nanoscopic characterization using conductive atomic force microscopy (C-AFM). The C-AFM characterization, in fact, demonstrated that zincblende defective AlN layer resulting in poorer insulating properties while the totally wurtzite AlN (0001) oriented films can be considered good insulator materials. This work has been supported by the European Union (NextGeneration EU), through the MUR-PNRR projects SAMOTHRACE (ECS00000022).

2:15pm AA1-WeA-4 Novel Low Temperature Thermal ALD of Aluminum Nitride Utilizing a Non-Metal Catalyst, *Sara Harris, M. Weimer, D. Lindblad, A. Dameron,* Forge Nano
Quality aluminum nitride (AlN) with conformal step coverage is crucial for the performance of current and next-generation microelectromechanical (MEMS) and microelectronic devices, including energy harvesters, ultrasonic transducers, high-frequency wide band communications, and power semiconductors.[1] AlN is widely utilized due to a unique combination of high piezoelectric quality factor (Q=5000 at 10 MHz),[2] high thermal conductivity (up to 320 W/m·K)[3] and a high dielectric constant (k= 9.0).[3] State of the art technology relies on AlN deposited via physical vapor deposition (PVD) or metal organic chemical vapor deposition (MOCVD); techniques unable to deliver the step coverage over high aspect ratio features necessary for device miniaturization. AlN deposited via ALD typically requires plasma or elevated temperatures (>350 °C) affecting process scalability and thermal budget, ultimately disincentivizing industry adoption.[4] In this work, AlN was grown at 285 °C via thermal ALD through the addition of a novel nonmetal catalyst during the nitride conversion step, referred to as a CRISP process. We demonstrate the power of CRISP on two different AlN processes: trimethylaluminum (TMA)/hydrazine (HZ) and TMA/monomethylhydrazine (MMH) and report a 15 % increase in refractive index (RI) for the TMA/HZ-CRISP process and binary off/on growth for the TMA/MMH-CRISP process. Normal ALD AlN films grown using TMA/HZ in the absence of a catalyst have an RI of 1.65 and GPC of 1.17 Å/cy. In comparison, AlN films grown via the novel TMA/HZ-CRISP process, using the nonmetal catalyst, have an RI of 1.95 and GPC of 1.50 Å/cy, as measured via spectroscopic ellipsometry. The partial pressure ratio between HZ and the nonmetal catalyst must be finely tuned to maximize AlN RI. To enhance understanding of the catalytic reaction pathways accessed by the CRISP process, ALD of TMA and MMH was conducted at 285 °C where the process is not kinetically favorable [4]. The absence of TMA/MMH film growth in traditional ALD fashion at 285 °C was confirmed, then a CRISP-based catalysis was introduced to facilitate proton transfer [4] and AlN was grown with RI of 1.62 and a GPC of 0.92 Å/cy. While under these conditions the TMA/MMH-CRISP film is of lower quality than those deposited with HZ/CRISP, this result highlights the ability of the nonmetal catalyst to enhance surface reactivity. GPC and RI improvement between a standard ALD process and the CRISP process is shown in Figure 1 for TMA/HZ and TMA/MMH. Additional characterization of the density and crystallinity of AlN films grown via the CRISP process will be discussed.

2:30pm AA1-WeA-5 Thermal and Plasma Enhanced ALD growth of functional Al₂O₃/AlN dielectric stacks for silicon carbide MOSFETs, *Raffaella Lo Nigro, B. Galizia, P. Fiorenza, E. Schilirò, F. Roccaforte,* Consiglio Nazionale delle Ricerche – Istituto per Microelettronica e Microsistemi (CNR-IMM), Italy
Over the last years, silicon carbide (4H-SiC) semiconductor has become suitable for high-power applications due to its superior properties compared with silicon, such as lower intrinsic carrier concentration, higher breakdown field, saturation velocity, and thermal conductivity. Nevertheless, there are still some open topics related to the exploitation of the full potentiality of this material and among them, the nature of the gate dielectric in metal-oxide-semiconductor-field effect-transistors (MOSFETs) is a crucial issue to be faced. In fact, the traditionally used SiO_2 dielectric suffers from low dielectric constant (≈3.9) compared to the one of 4H-SiC (≈9.7), so that, according to Gauss' law, the high breakdown field of 4H-SiC (3 MV/cm) cannot be fully exploited because of the earlier breakdown of SiO_2 layer. Consequently, high dielectric constant, large band-offset and good thermal stability as well as low density of defects are the ideal properties for gate dielectric in 4H-SiC power devices.

Aluminum oxide (Al₂O₃) possesses most of the ideal dielectric properties, nevertheless, did not demonstrate a better interface quality than SiO_2 layers. In this context, another high-κ insulator of interest is the aluminium

nitride (AlN) having not only high dielectric constant, but also a low lattice mismatch to 4H-SiC (~0.9%).These properties make it promising for a very good interface quality if epitaxially grown on (0001)4H-SiC.

In this work, a new solution is proposed: Al_2O_3/AlN bilayers were fabricated on 4H-SiC via ALD methods. In particular, thermal-ALD and PE-ALD processes of Al_2O_3 layers on AlN thin interfacial layer have been compared. Structural and electrical characterization of the two Al_2O_3/AlN bilayers obtained by T-ALD or PE-ALD depositions of the Al_2O_3 layers, are reported. Poor electrical behavior of the PE-ALD Al_2O_3/AlN bilayer has been correlated to its structural characteristics. In particular, the presence of degradation at the interface between plasma-deposited Al_2O_3 and AlN has been detected probably due to an oxidation interaction caused by oxygen plasma even at deposition temperature as low as 250°C.

By contrast, the structural and electrical properties of the T-ALD Al_2O_3/AlN bilayers showed promising characteristics such as a reduction of the oxide trapped charges (almost one order of magnitude down to 10^{11}-10^{12}), as well as of the interface traps density and an increase of dielectric constant (from 7.5 to 8.5) compared with a single Al_2O_3 reference layer. These preliminary results encourage the investigation of Al_2O_3/AlN bilayers as a candidate for future 4H-SiC power applications.

2:45pm AA1-WeA-6 Reduction of Defects at or Near ALD-Al_2O_3/GaN Interfaces for Improved Electrical Performance of GaN Power Devices, *Caleb Glaser*, B. Rummel, J. Klesko, M. Meyerson, P. Dickens, A. Binder, R. Kaplar, Sandia National Laboratories*; D. Feezell,* University of New Mexico
Wide bandgap (WBG) semiconductors, such as gallium nitride (GaN) and silicon carbide (SiC), are ideal candidates for high-power switching applications due to their high electron saturation velocity, lower conduction losses, and higher operating temperature capabilities compared to traditional silicon-based devices. GaN power devices often demonstrate clear technological improvements over their silicon counterparts and are competitive with SiC products in many high-power application spaces. However, there exist significant manufacturing challenges and reliability concerns associated with the complex architectures utilized by GaN-based designs, including the lack of a dependable thermally grown oxide. Atomic layer deposition (ALD) provides the opportunity to form reliable films for gate dielectrics or passivation layers in GaN structures. Electronic traps at or near the semiconductor/dielectric interface in MOS structures severely impact gate and channel performance by introducing leakage current pathways and threshold voltage instabilities as well as reduced channel mobilities. In addition, the formation of Ga_xO_y interlayers during the ALD formation of oxides like Al_2O_3 or HfO_2 may create additional defect sites leading to further deterioration of device performance.

This study explores the defect distributions at or near the ALD-Al_2O_3 interface in MOS gates and their impact on the electrical performance of GaN MOSCAPs and MOSFETs. Relative improvements to dielectric leakage, D_{IT} distributions, and capacitance-voltage hysteresis in MOSCAP structures have been analyzed to understand how the elimination of native oxides and reduction of potential defect sites improve electrical characteristics. Characterization of observable chemical bonds and surface morphology via XPS and AFM imaging and mapping shows the reduction of native oxide interlayers when exposed to precursor TMA cycling prior to Al_2O_3 film growth by ALD. The optimized deposition techniques and early detection methods for defect sites show an observable reduction of interface trap states, mid-gap trap states, and hysteresis measured by quasi-static C-V. Initial findings for improved semiconductor/dielectric interfaces on GaN MOSCAP devices were implemented into vertical GaN power MOSFETs and show significant improvements to device leakage currents and breakdown voltage. This marked increase in device performance follows the optimized ALD procedure that includes TMA cycling and reduces the calculated defect densities at or near the Al_2O_3/GaN interface through quasi-static C-V analysis.

3:00pm AA1-WeA-7 Fabrication of RuS2 Photodetector Via Post Sulfurization of Atomic Layer Deposition Ru Thin Film, *Jaehyoek Kim,* Yonsei University, Korea*; N. Tatsuya,* TANAKA Kikinzoku Kogyo K.K, Japan*; D. Kim,* Samsung Advanced Institute of Technology, Republic of Korea*; K. Yohei,* TANAKA Kikinzoku Kogyo K.K, Japan*; S. Chung,* Yonsei University, Korea*; S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; H. Kim,* Yonsei University, Korea
Near Infrared (IR) photodetectors are essential for many emerging applications in machine vision, health imaging, consumer electronics, and optical communications. Especially spectral responses of the photodetector at 940 nm are required for daylight applications due to the low interference intensity of the sunlight near that wavelength. Compound semiconductor materials have been mainly used in NIR photodetectors, but the exploration of novel semiconductor materials for excellent performance and effective fabrication processes continues to date.

Among the various emerging materials, the pyrite group semiconductors are promising candidates for optoelectronics. It belongs to the transition metal dichalcogenides (TMDs) family, and due to high absorption coefficient, extensive research on photovoltaic applications is being carried out to explore. In the case of Ru chalcogenides, RuS_2 is n-type semiconductor with suitable bandgap (0.8~1.4 eV) for NIR wavelength ranges and was identified as an optical and photoelectrode material with excellent environmental resistance and long lifespan. However, NIR photodetector studies based on RuS_2 to fabricate devices and measure photocurrent has not been conducted due to the difficulty of the RuS_2 thin film synthesis method.

In this report, RuS_2 film was synthesized based on Ru thin film deposition using atomic layer deposition (ALD) and post sulfurization process. Compared to sputtered Ru film, ALD of Ru film can be expected to improve the electrical and optical properties because ALD process provides uniform surface control and accurate thickness due to layer-by-layer deposition. Ru thin films with a thickness of 2, 4, and 6 nm were produced through ALD cycle control and post sulfurization were performed,and it was confirmed that 4 nm was optimized for RuS_2. After that, the RuS_2 characteristics of ALD Ru and Sputtered Ru were compared through several analyses such as XRD and XPS. The results suggest that the surface morphology of Ru thin film was important during sulfurization process, indicating that ALD Ru was excellent. We also fabricated RuS_2 photodetector with interdigitated comb-structured electrodes and measured at 940 nm NIR light. In this work, RuS_2 is proposed as a candidate material for the NIR photodetector and was the first to fabricate RuS_2 photodetector.

3:15pm AA1-WeA-8 Spatial Atomic Layer Deposition: A New Revolution in Ultra-Fast Production of Conformal and High-Quality Optical Coatings, *John Rönn,* P. Maydannik, S. Virtanen, K. Niiranen, S. Sneck, Beneq, Finland
Since its invention 50 years ago, atomic layer deposition (ALD) has shown tremendous performance in depositing thin film structures for various applications in physical, chemical, biological, and medical sciences. Due to the unique layer-by-layer growth mechanism of ALD, thin films with exceptional uniformity, conformality and quality can be deposited not only on planar substrates, but also on the most complicated surfaces. Despite its superior advantages, traditional ALD, or temporal ALD, suffers from relatively low deposition rates (20-50 nm/h), which has greatly limited ALD's application in many systems where thin films with thicknesses of several hundreds or even microns are required. Such examples are often found in optical coatings that are widely used in our everyday lives in the form of self-driving cars, augmented reality goggles or mobile phones, to name a few.

In this work, we present our latest achievements with the novel C2R spatial plasma-enhanced rotary ALD system. The results include ultra-fast production of SiO_2, Ta_2O_5 TiO_2, HfO_2 and Al_2O_3 with deposition rates reaching up to 2 μm/h. In addition, we show that the deposition of these films can be controlled in such a way that no coating induced stress is obtained on the substrate, ultimately allowing extremely thick layer configurations to be deposited for optical applications. Finally, we show that these films exhibit low optical losses which make them very advantageous for novel optical applications where conformal, thick, and low-loss coatings are highly desirable.

ALD Applications
Room Hall 3D - Session AA2-WeA

Emerging: Optics/Optoelectronics
Moderators: Tero Pilvi, Picosun Oy, **Tania Sandoval**, Technical University Federico Santa Maria

4:00pm AA2-WeA-11 Deposition and Characterization of Electro-Optic ALD K(Ta$_x$,Nb$_{1-x}$)O$_3$ Films for Photonics, *Eric Martin,* Ohio State University*; J. Bickford,* Army Research Laboratory*; H. Sønsteby,* University of Oslo, Norway*; R. Hoffman,* Army Research Laboratory*; R. Reano,* Ohio State University
Electrooptic (EO) materials are critical for optics and photonics, enabling fast and dynamic control propagating light.In particular K(Ta$_x$,Nb$_{1-x}$)O$_3$ (KTN) stands as a unique EO material in that it possesses an extremely high quadratic (Kerr) EO coefficient. KTN is a solid solution of $KTaO_3$ and $KNbO_3$ perovskites with a Curie temperature (T_c) that is defined by the Ta:Nb

ratio.Bulk KTN crystals have shown record high Kerr nonlinearity of greater than 2.2 x 10^{-14} m^2/V^2 when thermally tuned near T_c.However, difficultly in fabrication of KTN crystals greater than 1cm^2 in area has limited applications to small varifocal lens and beam deflectors.Recent advancements in ALD of KTN utilizing alkoxide precursors and O$_3$ as the oxidant has shown precise composition control and excellent crystallinity on both (LaAlO$_3$)$_{0.3}$(Sr$_2$TaAlO$_6$)$_{0.7}$ (LSAT) and MgAl$_2$O$_4$ (MAO) substrates.ALD KTN films open exciting new possibilities for both bulk and integrated optical building blocks, including tunable filters, reflectors, modulators, phase shifters, and grating emitters.In this work, we investigate the deposition of crystalline KTN on a variety of substrates including LSAT, MAO, MgO, and Si. Our approach encompasses several facets. We begin by depositing KTN thin films using alkoxide precursors and O$_3$ as the oxidant. The deposited films are characterized for their optical properties using spectroscopic ellipsometry. We determine the crystallinity of the films through x-ray diffraction (XRD) and evaluate the composition via x-ray fluorescence (XRF). We further probe the dielectric response of the films and determine T_c the through capacitance measurements. This includes utilizing interdigitated capacitors (IDCs) and metal-oxide-semiconductor (MOS) capacitors for precise temperature-dependent characterization. Additionally, we investigate the EO properties of KTN films as a function of temperature and composition. This is achieved using specialized silicon Photonic Integrated Circuit (PIC) test chips, comprised of a Mach-Zehnder interferometer trenched for KTN deposition with an integrated photodetector. For the first time, we report the optical, dielectric, and electrooptic properties of ALD KTN thin films.

4:15pm **AA2-WeA-12 Advances in Plasma-based Atomic Layer Processing of AlF$_3$ for the Passivation of FUV Mirrors**, *Virginia Wheeler, M. Sales, D. Boris,* Naval Research Laboratory; *L. Rodriguez de Marcos,* Catholic University of America and NASA Goddard Space Flight Center; *J. del Hoyo,* NASA Goddard Space Flight Center; *A. Lang, S. Walton,* Naval Research Laboratory; *E. Wollack, M. Quijada,* NASA Goddard Space Flight Center

Efficient ultraviolet mirrors are essential components for UV astronomy. While aluminum mirrors with stable and reliable fluoride-based passivation layers are commonly used, the optical performance is still insufficient for systems where several reflections are required. We previously demonstrated the feasibility of a new, room temperature plasma process based on a benign SF$_6$ electron beam (e-beam)-generated plasma to simultaneously remove the native oxide and form an AlF$_3$ layer with tunable thickness [1]. This produces Al-mirrors with high FUV reflectivity (R≈90% at λ=121nm) and improved durability. Plasma-enhanced atomic layer deposition (PEALD) is a known low temperature, highly conformal coating process which has previously been shown to produce AlF$_3$ films [2], though little has been reported on their performance in FUV applications. In this work, we focus on optimizing a PEALD AlF$_3$ process using a remote ICP plasma and developing a new hybrid approach combining the e-beam-generated plasma and ICP processes. We will provide a detailed analysis of AlF$_3$ film materials properties and FUV optical performance produced by each approach individually and combined.

PEALD AlF$_3$ films were deposited using trimethylaluminum and SF$_6$ plasma precursors in a Veeco Fiji G2 reactor custom fitted with an on-axis cylindrical e-beam-generated plasma to replicate the self-fluorination process directly on an ALD reactor. ALD windows were optimized using *in situ* ellipsometry directly on Al substrates and supplemented with post-deposition x-ray photoelectron spectroscopy, atomic force microscopy, transmission electron microscopy and FUV measurements to elucidate process-structure-property relationships. Plasma diagnostics, including optical emission spectroscopy and Langmuir probe measurements, were also conducted on the reactor to correlate ion fluence and ion energy to resulting film properties. PEALD AlF$_3$ films with F/Al ratios of 2.92-2.97, < 2 at% oxygen, and surface roughness similar to starting Al-mirrors were attained at lower plasma power (100W), high SF$_6$/Ar ratios (≥ 0.5) and gas flows (> 30sccm). However, the FUV properties of these films are still inhibited by the native oxide interface that cannot be adequately treated with remote ICP plasma alone. Initial films combining an *in situ* e-beam-generated plasma for fluorine passivation of the Al mirror interface with the optimum PEALD produced better FUV performance in the 100-190 nm region. Full detailed characterization of this hybrid approach will be discussed.

[1] L.V. Rodriguez de Marcos, et al. Opt. Mater. Express 11, 740-756 (2021)

[2] M.F.J. Vos, Appl. Phys. Lett. 111, 113105 (2017)

4:30pm **AA2-WeA-13 Plasma-Enhanced Atomic Layer Deposition with RF Substrate Biasing to Tune the Performance of Superconducting Nanowire Single-Photon Detectors in the Mid-Infrared**, *Ciaran Lennon,* Oxford Instruments Plasma Technology, University of Glasgow, UK; *D. Morozov,* University of Glasgow, UK; *Y. Shu,* Oxford Instruments Plasma Technology, UK; *H. Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands; *K. Hore,* Oxford Instruments Plasma Technology, UK; *R. Hadfield,* University of Glasgow, UK

Superconducting nanowire single-photon detectors (SNSPDs) offer field-leading time-correlated single photon detection in the infrared, with ultrafast timing jitter, near-unity internal detection efficiency and low dark count rates [1]. Extending the performance in the mid-infrared has been a focus in the field, potentially expanding the range of SNSPD applications in areas like exoplanet spectroscopy and LIDAR [2,3].

Previous work on mid-infrared SNSPDs has focused on amorphous superconducting materials (WSi) owing to their lower superconducting energy gap (Δ), demonstrating saturated internal detection efficiency up to 29 μm [4,5]. However, amorphous materials have lower Tc, requiring device operation at < 2K with bulky, energy-intensive cryocoolers. Crystalline metal nitrides, like NbN and NbTiN, are a promising alternative, with T$_c$ > 10 K, enabling device operation at > 2 K, although with higher Δ. Lowering Δ has been shown to increase the detection efficiency in the mid-infrared [5]; therefore, tuning Δ for NbN and NbTiN could be a promising approach.

Controlling the ion energy in the plasma-enhanced atomic layer deposition (PEALD) process using RF substrate biasing can influence various material properties such as crystallinity, composition and stress [6]. Recent work has also shown that the superconducting properties of metal nitride thin films can be tuned using RF substrate biasing [7,8], as well as enhancing the uniformity, making it an ideal technique for the development of large-area SNSPD arrays. Consequently, we have used PEALD with RF substrate biasing to develop NbN and NbTiN thin films tuned for mid-infrared SNSPDs. We report on the electrical and superconducting properties of the ultrathin films and discuss the fabrication, electrical transport properties and optical testing of fabricated SNSPDs, with their performance benchmarked from 1.5-4 μm.

Overall, this study highlights the potential of PEALD with RF substrate biasing for developing NbN and NbTiN thin films for SNSPDs tuned for mid-infrared photon counting applications, with scope to develop large-area SNSPD arrays.

[1] Morozov D. V., *et al.*, *Contemp Phys* **62** 69-91

[2] Wollman E. E., *et al.*, J Astron Telesc Instrum Syst **7** 1-10

[3] Taylor G. G., *et al.*, Opt Express **27** 38147

[4] Verma V. B., *et al.*, APL Photonics **6**

[5] Taylor G. G., *et al.*, Optica **10** 1672

[6] Faraz T., *et al.*, ACS Appl Mater Interfaces **10** 13158-80

[7] Peeters S. A., *et al.*, Appl Phys Lett **123** 132603

[8] Lennon C. T., *et al.*, Materials for Quantum Technology **3** 045401

ALD Applications
Room Hall 3E - Session AA3-WeA

Display Applications
Moderator: Marianna Kemell, University of Helsinki

4:00pm **AA3-WeA-11 Atomic Layer Deposition for Stable On-Chip Quantum Dot LEDs: Hybrid Quantum Dot Pockets**, *Robin Petit, R. Özdemir, H. Van Avermaet, J. Kuhs, A. Werbrouck, J. Dendooven, Z. Hens, P. Smet, C. Detavernier,* Ghent University, Belgium

The latest advancements in displays include micro-LEDs with chip sizes < 100 μm that are used as subpixels. To avoid color filters and bulky layers with separate color converter devices, the color converter is preferably deposited on-chip.

Their narrow emission spectrum and size-tunability make quantum dots (QDs) attractive as color converters in displays. The best alternative to Cd-based QDs are InP-based QDs, owing to their ability to emit the full spectrum of colors, their structural integrity and low toxicity[1]. However, non-radiative pathways from defect-related traps or interactions with the environment (H$_2$O, O$_2$) can be detrimental to the luminescence efficiency.

State-of-the-art hybrid barriers are explored to safeguard the QD luminescence. Metal oxides grown by atomic layer deposition (ALD) have

shown potential when paired with organic layers, such as those deposited by molecular layer deposition[2]. The defect-free nature and conformality of the coatings is unique to ALD, making it an ideal technique for barrier applications.

This study investigates ALD for stable on-chip QD LEDs as follows: **(a) Understanding the optical response** of core/multi-shell InP/ZnSe/Zn(Se,S)/ZnS QDs to precursors (TMA, TDMAT, DEZ), reactants (H_2O, O_3), plasmas (Ar, H_2, O_2) and full ALD processes (Al_2O_3, TiO_2, ZnO) using a home-built in situ photoluminescence setup[3]. Results show that the QDs are highly susceptible to degradation during the ALD process (Fig. 1). **(b) Characterizing ALD growth** (Al_2O_3) **on polymer substrates** (Kraton) by spectroscopic ellipsometry and Fourier transform infrared spectroscopy. Island growth is identified as the dominant growth mode and is linked to the copolymeric structure of Kraton (Fig. 2). It is observed the stability of the QDs during ALD is vastly improved by polymer embedding. **(c) Fabrication of pick-and-place, hybrid QD pockets** using a digital light processing setup as a demonstrator for on-chip QD LEDs (Fig. 3)[4]. By combining the on-chip design of the QD pockets and seamless encapsulation of the QDs by a polymer (thiol:ene) with the barrier performance of ALD coatings, this work aims to contribute to the development of stable QD LEDs for displays. **(d) Examining the long-term stability** of (ALD coated) pristine QDs, polymer-embedded QDs, and QD pockets through accelerated aging tests using a humidity chamber. The hybrid QD pockets show superior stability demonstrating their potential for QD LEDs.

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4:15pm AA3-WeA-12 A Comparative Study on Cation distribution effects in Heterogeneous channel IGZO TFTs via Atomic Layer Deposition Supercycle Design, *Hye-Jin Oh, H. Kim,* Hanyang University, Korea*; C. Park,* Hanyang University, Republic of Korea*; J. Park,* Hanyang University, Korea

Oxide semiconductors (OSs), known for their high mobility, large-area uniformity, low temperature processability, low off current, are garnering interest in display applications.[1] To apply in various fields, it is essential to enhance the electrical properties of OS thin-film transistors (TFTs). Atomic layer deposition (ALD) a-IGZO has been reported to exhibit improved electrical properties due to increased packing density compared to the conventional sputtering method.[2] Sputtering uses a target mixed with each element to form a homogeneous thin film, but supercycle-based ALD forms a relatively heterogeneous thin film. In this regard, it is crucial to consider the cation distribution resulting from the ALD supercycle configuration in multicomponent OSs.

In this study, we aimed to compare surface and bulk compositions based on cation distributions by reversing the supercycle sequence of the indium (In), gallium (Ga), zinc (Zn) elements in IGZO: **A (In (14) -Ga (3) -In (14) -Zn (4)), A'(Zn (4) -In (14) -Ga (3) -In (14))**. As a result, the surface composition (XPS) of channels A and A' was significantly higher for the element located in the last order of the supercycle sequence (A: Zn-rich surface, A': In-rich surface). However, the XRF analysis indicated a similar bulk composition for A and A', and notable distinctions in physical properties were not evident. Despite considerable differences in surface composition between A and A', the TFT electrical properties did not show substantial variation, but there was a significant distinction in reliability. The outcomes suggest that the bulk composition has a more pronounced influence on the electrical properties of the TFTs, and the composition ratio at the surface acting as the back channel has a significant impact on stability. The A' TFT, with an In-rich surface, experiences a hump phenomenon caused by the formation of a parasitic channel on the back channel, leading to performance degradation. Our research proposes that the cation distribution in ALD-based multicomponent heterogeneous channel TFTs can affect the electrical properties and reliability results, depending on the device structure.

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4:30pm AA3-WeA-13 Characteristics of PEALD IGZO Films Using Tetrahydrofuran-Adducted In & Ga Precursors, *S. Lee, S. Jeon, S. Lee, Y. Kwone, Y. Im, T. Byun,* **Sungchul Kim,** DNF Co. Ltd., Republic of Korea

As the down-scaling of semiconductor materials, silicon compatible emerging materials have extensively researched for next generation display and 3D structured devices. In particular, oxide semiconductors are considered a promising candidate for backplane applications in display. Among them, indium-gallium-zinc oxide (IGZO) using plasma enhanced atomic layer deposition (PEALD) has excellent properties, like high mobility, low leakage current, high transparency and low temperature processability. However, conventional precursors for IGZO still have some problems to solve such as low deposition rate, low thermal stability and high price.

In this study, we developed indium precursor (Trimethylindium Tetrahydrofuran, DIP-4) and gallium precursor (Trimethylgallium Tetrahydrofuran, DGP-2) to overcome the shortcomings of the conventional In & Ga precursors. ALD characteristics of the films deposited using the newly developed the precursors were confirmed through the source feeding time saturation and linearity. Furthermore, the incubation time of In, Ga and Zn oxide films according to the different bottom layer was respectively verified and calculated using the developed DIP-4, DGP-2 and commercially used DEZn. In order form a multilayer IGZO thin film, application of the incubation factors at IGZO process were experimentally demonstrated. Thickness of the IGZO films can be easily controlled through modulation of the incubation factors. The physical and chemical properties of the films were analyzed by X-ray diffraction, X-ray reflectrometer, X-ray photoelectron spectroscopy, transmission electron microscope.

ALD Fundamentals
Room Hall 3A - Session AF1-WeA

Growth and Characterization: *In-situ* and *in-vacuo* Analysis, Surface Science of ALD I

Moderators: Seán Barry, Carleton University, Canada, **Simon D. Elliott**, Schrödinger

1:30pm AF1-WeA-1 Triggering Nucleation of Pt ALD through UV-illumination, *J. Santo Domingo Peñaranda,* **Jolien Dendooven,** Ghent University, Belgium*; V. Miikkulainen,* Aalto University, Finland*; S. Klejna,* AGH University of Science and Technology, Poland*; E. Solano,* ALBA synchrotron, Spain*; M. Rosenthal,* ESRF, Grenoble, France*; Z. Hens, C. Detavernier,* Ghent University, Belgium

ALD of noble metals on oxides is marked by the growth of 3D islands rather than a uniform 2D layer in the initial growth stages. A relatively large number of ALD cycles is often required to achieve coalescence of the growing islands into a continuous layer, posing limits to the deposition of thin metal films. To obtain layer closure at lower thicknesses, a larger density of nuclei formed on the substrate surface (#nuclei/cm^2) is desired.

For MeCpPtMe$_3$-based Pt ALD, strategies to enhance the nucleation include using N$_2$-plasma as reactant instead of O$_2$ [1], exposing the substrate to alkylated precursors prior to Pt deposition [2], and using electron excitation of the Pt precursor [3]. Here, we implement UV-illumination as an external trigger during MeCpPtMe$_3$-O$_2$ ALD and study the Pt uptake and nucleation process *in situ* via X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) at the ESRF synchrotron.

With 365 nm illumination turned on continuously during the ALD process, in situ growth curves (Fig. 1) reveal a significant increase in Pt deposition during the incubation period at all temperatures tested. Depositions in which a number of Photo-ALD cycles is followed by thermal ALD (Fig. 2) also show a drastic increase in Pt uptake, even if only few Photo-ALD cycles are carried out, confirming a crucial role for the UV-light in the nucleation. The size and areal density of the nuclei is extracted for samples with the same Pt loading (#Pt atoms/cm^2) (Fig. 3). Remarkably, a larger amount of smaller islands is formed with Photo-ALD, indicative of an increased nucleation density.

Next, the timing of the UV-illumination in the ALD cycle is varied to understand the effect of light-assistance during each ALD step. UV-illumination during the MeCpPtMe$_3$ exposure is required to achieve growth enhancement, suggesting that the precursor is activated in the gas phase prior to adsorption. We hypothesize that the UV-light assists in the dissociation of the Pt-Me bonds [5], enabling a larger Pt uptake on the surface.

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In summary, UV-light can trigger the nucleation of Pt ALD, leading to a larger nucleation density and faster layer closure compared to conventional thermal ALD. While this in itself offers great opportunities for ALD of thin metal films, the Photo-ALD approach also holds promises towards selective deposition for micropatterning.

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1:45pm AF1-WeA-2 Reaction Pathway of Copper Atomic Layer Deposition via Time-of-Flight Mass Spectrometry, *Camilla Minzoni, K. Mackosz, C. Hain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Frege,* TOFWERK AG, Switzerland*; I. Utke, P. Hoffmann,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Atomic Layer Deposition (ALD) has emerged as one of the most promising technique for depositing conformal and uniform copper thin film, especially for application in electronic devices [1].

Despite a comprehensive understanding of ALD mechanisms in metal oxides, limited theoretical and *in situ* experimental work has been dedicated to unraveling the reaction mechanisms of copper and related metals. The extension of ALD to elemental metals presents distinctive challenges, primarily attributed to the lack of the mechanistic understanding of the ongoing surface reactions [2].

Time-of-Flight Mass Spectrometry (ToFMS) has become a powerful tool for addressing these issues, providing unique advantages in terms of high sensitivity and resolving power, rapid data acquisition, ability to detect species over a wide mass range and real-time tracking of surface reactions and volatile byproducts.

This study presents *in situ* ToFMS monitoring to investigate the gas-phase mechanism involved in the ALD process of copper through transmetalation, using dehydrated Cu(hfac)$_2$ (CuC10H2F12O4) with diethylzinc DEZ (Et2Zn) being the reducing agent.

Lee et al. [3] previously proposed a transmetalation reaction mechanism using an analogous copper complex and DEZ. The mechanism involves a ligand exchange step between the copper complex and DEZ, leading to the formation of the volatile byproduct Zn(hfac)$_2$ (ZnC10H2F12O4), along with the generation of copper alkyl surface species. These copper alkyl species rapidly undergo reductive elimination, producing copper metal and butane (C4H10) [4] (Fig. 1).

During the monitoring of the ALD cycles with ToFMS, the theoretically anticipated byproducts from the transmetalation reaction were detected (Fig. 2). The results identifying these byproducts are the first of their kind under vacuum ALD conditions, supporting also the theoretical calculations and solution-based of analogous reactions [5-6].

The combination of ALD and ToFMS is therefore proving to be a powerful method for a depth understanding of complex ALD reaction mechanisms at molecular level that would be challenging by other means.

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2:00pm AF1-WeA-3 *in vacuo* **Cluster Tool for Studying Reaction Mechanisms in ALD and ALE Processes**, *Marko Vehkamäki, M. Chundak, H. Nieminen, M. Putkonen, M. Ritala,* University of Helsinki, Finland

ALD and ALE processes are solely dependent on the chemical reactions occurring on the substrate surface. These surface reactions define the outcome of each process and can set critical challenges on the process development and integration. Studying the chemical reactions is hence of utmost importance to fully understand the growth and etch processes and exploit the advantages ALD and ALE have to offer.

The best ways to study reaction mechanisms in ALD and ALE processes is to do the measurements without exposing the film to air, that is, either *in situ* or *in vacuo*. A cluster tool which allows a variety of ways to study reaction

mechanisms in nearly all kinds of process chemistries has been set up in HelsinkiALD laboratory. In this tool, a commercial flow-type ALD reactor is connected directly to a set of ultra-high vacuum analysis chambers. After interrupting the process at selected point the substrate can be transferred *in vacuo* straight from the ALD reactor to surface analysis. The chemical composition of the surface, including also reaction intermediates on the film, can be investigated after each precursor pulse individually. With this information, the overall film growth mechanism can be resolved.

The newest addition to the cluster tool is a low-energy ion scattering (LEIS) instrument. LEIS has the ultimate surface sensitivity as it distinguishes the outermost atom layer from the others. This resolution is important in distinguishing reaction intermediates from the rest of the surface and in analyzing the closure of the thinnest films. X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and *in situ* quartz crystal microbalance (QCM) have already been utilized effectively in reaction mechanism studies on ALD of Al$_2$O$_3$, noble metals Pt and Ru, and ALE of Ta and Mo. Additionally, the cluster tool contains *in vacuo* ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), and ultraviolet photoelectron spectroscopy (UPS). There is also an ellipsometer for *quasiin situ* measurements in the ALD chamber. As the system contains genuine flow-type ALD reactor, reaction mechanisms can be solved without compromising true ALD conditions.

2:15pm AF1-WeA-4 Understanding the Dual-Source Behavior of LiHMDS for Si-Free Li-Containing Films, *Meike Pieters, L. Bartel, C. van Helvoirt, M. Creatore,* Eindhoven University of Technology, The Netherlands

The electrochemical stability of interfaces is key to long-lasting and safe Li-ion batteries. To study these interface processes, ALD can deliver thin film model systems of electrodes. For example, the behavior of Ni-rich LiNi$_x$Mn$_y$Co$_{1-x-y}$O$_2$ cathodes can be understood by investigating LiNiO$_2$ thin films due to the similar electrochemical properties. Moreover, the control that ALD provides over film composition and crystal orientation allows to study how those material properties influence the interface stability. To grow LiNiO$_2$ by ALD, lithium hexamethyldisilazide (LiHMDS) is preferred over the widely-used LiO^{t}Bu because of its lower melting point of 70ºC, but the presence of silyl groups can result in the undesired incorporation of Si. Previous work proposes that Si is incorporated during both precursor and O$_2$ plasma steps in the ALD cycle [1]. However, processes in which the LiHMDS dose is followed by a H$_2$O pulse can yield Si-free films [2,3], indicating that the co-reactant plays a major role in the Si incorporation.

To shed light on the reaction mechanisms of LiHMDS and the two co-reactants, we carry out in-situ growth studies by spectroscopic ellipsometry and mass spectrometry (QMS) [4]. The O$_2$ plasma process shows linear growth and the film contains 16 at.% Si according to XPS, but the H$_2$O process results in bulk-driven growth and Si-free films. QMS shows that the difference between the processes lies in the reaction products during the co-reactant step: H$_2$O removes the HMDS ligands of physisorbed LiHMDS via a proton exchange reaction, whereas the O$_2$ plasma combusts HMDS. The redeposition of Si-containing combustion products during the plasma step is presumably the origin of the dual-source behavior of LiHMDS.

We also include a H$_2$ plasma step following the O$_2$ plasma step, with the hypothesis that H radicals can etch the incorporated Si. This process exhibits bulk-driven growth and the grown films are, as expected, Si-free and have a Li$_2$O composition. QMS confirms the release of SiH$_x$-species during the H$_2$ plasma step. Interestingly, the growth behavior and film composition remain the same when the order of the O$_2$ and H$_2$ plasmas is reversed. The QMS results in this case indicate that H$_2$ plasma removes the HMDS ligands and thereby prevents Si incorporation in the subsequent O$_2$ plasma step.

Overall, this work shows that the co-reactant controls the reaction mechanism, and therefore the dual-source behavior, of LiHMDS. These insights can aid the fabrication of Si-free LiNiO$_2$ films.

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2:30pm AF1-WeA-5 ALD of Two-Dimensional Gallium Sulfide: Understanding the Nucleation and Strain Evolution During Growth, *O. Massmeyer, R. Günkel, S. Kachel,* Philipps Universität, Germany*; P. Klement,* Justus Liebig University Giessen, Germany*; J. Belz,* Philipps Universität, Germany*; S. Chatterjee,* Justus Liebig University Giessen, Germany*; M. Gottfried, **Kerstin Volz**,* Philipps Universität, Germany

Two-dimensional (2D) materials are gaining great attention due to their extraordinary thickness-dependent properties. The layered III-VI semiconductors such as GaS and GaSe show a unique band structure. Furthermore, 2D GaS and GaSe have a bandgap in the UV region, which makes them candidates for several LED and detector concepts. Moreover, the composition tuning of multilayer GaS_xSe_{1-x} alloys allows for establishing bandgaps between 2.0 and 2.5 eV.

Hence, group III-chalcogenides are promising materials for next-generation optoelectronic applications, as they even reach these properties with comparably little use of material. Typical preparation routine for 2D materials, however, is the mechanical exfoliation, which is no suitable technique when applications are aimed for. Hence, we establish a pulsed growth regime using metal organic precursors to find suitable growth routines for 2D materials using a well-accepted growth technique. The samples are characterized by means of Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Raman spectroscopy, X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and Transmission Electron Microscopy (TEM) as well as several optical spectroscopy techniques.

The ALD (Atomic Layer Deposition) scheme is needed due to prereactions of the di-*tert*-butyl-sulphide (DTBS) and tri-*tert*-butyl-gallium (TTBGa) precursors on the surface. This results in the formation of 2D, closed films instead of 3D structures containing liquid Ga on the surface. The growth of a 2D film is enabled by a specific interface reconstruction between the sapphire and the GaS.

The presentation will summarize our current understanding of the nucleation and ALD growth of group III-chalcogenides by systematic variation of different growth parameters such as temperature, chalcogen/group III gas phase ratio and deposition sequences and correlate the findings to optoelectronic properties of the layers.

2:45pm AF1-WeA-6 Self-Limiting Deposition of Copper from Copper Beta-Diketonates and Plasma Electrons, *Premrudee Promdet, P. Niiranen, A. Haridas Choolakkal, D. Lundin, H. Pedersen,* Linköping University, IFM, Sweden

We have recently demonstrated how films of elemental metals can be deposited using free electrons from a plasma discharge as reducing agents.[1] We refer to this process as electron CVD (e-CVD). We will here demonstrate e-CVD of Cu using plasma electrons and copper beta-diketonates precursor; we will also show that the deposition chemistry appears to be self-limiting. Hence, we suggest that this might be an e-ALD process.

In this study, a positive bias is applied to the substrates to attract plasma electrons to the surface. The copper precursors and the plasma electrons were supplied in pulses separated by argon purge steps. The deposition was monitored *in situ* by a QCM sensor specially developed for e-CVD[2]. Self-limiting deposition was found from the mass gain per deposition cycle for the time of precursor pulse, plasma exposure and purge. X-ray photoelectron spectroscopy show the formation of fluorinated copper species, suggesting some level of redeposition of ligand fluorine to the copper surface. We found that the residual fluorine could be removed by further plasma exposure. A plausible explanation supported by optical emission spectroscopy and mass spectroscopy is offered on the formation of volatile compounds as byproducts from the longer plasma exposure. Based on these results, a possible surface chemical mechanism will be discussed.

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3:00pm AF1-WeA-7 Exploration of Nucleation Phenomena in Ultra-Thin ALD Films on NMC 811 Substrates: An in Situ Quartz Crystal Microbalance Study, *Léo Lapeyre, L. Pethö, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; P. Raynaud,* LAPLACE, France*; I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Ultra-thin films deposited by ALD have emerged as essential components in improving the performance and stability of Li-ion battery systems. Particularly, the utilisation of ultra-thin films as artificial solid electrolyte interfaces (SEIs) holds significant promise for enhancing battery efficiency and lifespan. However, the accurate characterisation of these films by ex situ methods presents significant challenges, primarily due to their low thicknesses which provides low signal-to-noise ratiosand potential contamination from air exposure. Additionally, the substrate's influence on film properties remains a critical but often overlooked factor. Many studies rely on silicon substrates for process development and film characterization, yet the disparities between silicon and actual battery substrates, such as NMC 811, can significantly impact film growth and characteristics. Among others aspects, unsaturated surface coverage, non-linear growth per cycle (GPC), or compositional variations during early stage growth may result from an ALD process not specifically optimized for the particular substrate in use. Consequently, these variations can adversely affect battery performances.

To address these challenges, we use in situ Quartz Crystal Microbalance (QCM) techniques with NMC 811-coated QCM crystals to achieve closer-to-application conditions and overcome limitations associated with ex situ methods. This approach enables us to investigate nucleation phenomena and growth kinetics of ultra-thin films with fine precision [2], providing a better understanding of the substrate's influence on film properties and facilitating the development of tailored deposition strategies for enhanced battery performance.

Our study encompasses the deposition of various materials, including SnO2 and LiNbO3, using both ALD and PE-ALD techniques. We aim to compare the influence of deposition methods (thermal and plasma ALD) on the early-stage growth dynamics of films and explore the effects of deposition parameters (such as temperature, precursor's exposure time and number of cycles) on growth behaviours. Ultimately, we seek to optimize the deposition process to minimize non-linear growth and enhance film quality.

Finally, we will assess the electrochemical performance of NMC 811 electrodes coated with SnO2 and LiNbO3 films, investigating their capacity retention, cycling stability, and rate capability. Through this comprehensive analysis, we strive to advance our understanding of ultra-thin film deposition processes and their impact on battery performance, ultimately contributing to the development of high-performance energy storage solutions.

3:15pm AF1-WeA-8 The Role of the Oxidizing Co-Reactant in Pt Growth by Atomic Layer Deposition Using MeCpPtMe₃ and O₂/O₃/O₂-Plasma, *Jin Li,* Ghent University, Belgium, China*; S. Klejna,* AGH University of Krakow, Poland*; M. Minjauw, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Atomic layer deposition (ALD) of Pt using $MeCpPtMe_3$ and $O_2/O_3/O_2$-plasma (O_2^*) at 300°C is investigated with *in vacuo* X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) to gain a better understanding of the Pt growth mechanism.[1] Most notably, the chemical state of the surface Pt atoms and the role of surface O species in Pt growth are revealed. In the $MeCpPtMe_3/O_2$ process, the surface Pt atoms remain in a metallic Pt^0 state throughout the ALD cycle, and the surface O species generated by the O_2 exposure only exist as unstable adatoms, desorbing in vacuum. As for the O_3/O_2^* processes, the surface Pt layer is oxidized to a mixture of Pt^0, $Pt^{2+}O$ and $Pt^{4+}O_2$ upon O_3/O_2^* exposure and then fully reduced to Pt^0 during the precursor exposure. Surface Pt oxides are stable in vacuum but can be reduced by hydrocarbon vapors. DFT reveals differences in the combustion mechanism for Me vs. Cp species, during the metal precursor and co-reactant pulses. Quantification analysis shows that the O_3/O_2^* processes have a much higher surface O species content than the O_2 process after the co-reactant exposure, favoring precursor ligand combustion over dehydrogenation in the next precursor exposure and leading to lower surface C density after the precursor pulse. Regarding the surface C species, apart from common $-C_xH_y/-Cp$ groups, $-C_x$ is recorded as a highly dehydrogenated product only in the $MeCpPtMe_3/O_2$ process. For all processes, no C-O/C=O or -OH group is identified by *in vacuo* XPS, in line with DFT energetics. Importantly, the differences in the surface O content do not significantly affect the growth per cycle. Moreover, the $MeCpPtMe_3/O_2$ process with surface O species and a tailored $MeCpPtMe_3/O_2$ process without surface O species, both at 300°C, yield nearly identical growth rates and as-deposited Pt with the same chemical state. This indicates that surface O species present before the precursor exposure have limited impact on the overall Pt growth, in contrast to previous assumption.

KEYWORDS: In vacuo XPS; DFT; ab initio thermodynamics; surface reaction mechanism; Atomic layer deposition; Pt; growth mechanism; combustion of hydrocarbons mechanism

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1 J. Li, S. Klejna, M. M. Minjauw, J. Dendooven and C. Detavernier, *J. Phys. Chem. C,*DOI:10.1021/acs.jpcc.3c07568.

ALD Fundamentals
Room Hall 3A - Session AF2-WeA

Growth and Characterization: *In-situ* and *in-vacuo* Analysis, Surface Science of ALD II

Moderators: Markku Leskelä, University of Helsinki, Finland, **Mikko Ritala**, University of Helsinki

4:00pm **AF2-WeA-11 In vacuo XPS Growth Studies During ALD of ErNiO₃**, *Matthias Minjauw,* Ghent University, Belgium*; A. Illiberi, M. Givens,* ASM, Belgium*; A. Leonhardt, I. Issah, L. Bottiglieri,* ASM, Finland*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Rare-earth nickelates (RNiO₃, with R = rare earth element) have a broad range of unique and tunable physical properties, making them relevant for future applications in electronics, electrocatalysis, solid oxide fuel cells, electrochromic windows and microelectromechanical systems. As a result, several RNiO₃ ALD processes (R = La, Nd) have been reported, and the general approach is to combine two binary ALD processes for R_xO_y and NiO in supercycles.[1-3] As two distinct ALD processes are combined into one ALD process, several non-idealities may occur, such as a larger impurity content than for the binary processes, nucleation effects leading to irreproducibility issues, and unexpected high/low growth leading to deviating compositions.[4]

In this work, we combined the ALD NiCp₂/O₃ and Er(MeCp)₃/O₃ processes at 300°C using the supercycle approach, leading to Er$_x$Ni$_y$O$_z$ films with low impurity content. Figure 1a shows the growth per cycle (GPC) of the ALD process as a function of the NiO cycle ratio. Ideally, a linear curve should be obtained between the GPC values for the binary processes, but this is clearly not the case. In Figure 1b, it is seen that the Ni atomic concentration as found by *in vacuo* XPS is also much lower than expected based on the rule of mixtures.[4]

To investigate the origin of these non-idealities, *in vacuo* ALD-XPS nucleation studies were conducted, and a selection of XPS data is shown in Figure 2. Although an Er signal is visible from the first Er(MeCp)₃-pulse on an ALD NiO substrate, it takes ~ 4 cycles of the NiO process to get a clear Ni signal on an ALD Er₂O₃ surface. In Figure 3, a plot is shown of the Ni and Er atomic percentage as a function of ALD cycles, obtained by quantifying the XPS data. The fact that there is a nucleation delay for NiO growth on Er₂O₃, but not for Er₂O₃ on NiO, explains the non-idealities described above. The present XPS data hint that incomplete surface reactions of the NiCp₂/O₃ process on the carbon-rich ALD Er₂O₃-surface are at the basis of this nucleation delay, with more research currently ongoing to elucidate this.

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4:15pm **AF2-WeA-12 Surface Chemistry of Aluminum Nitride ALD**, *Pamburayi Mpofu, H. Hafdi, H. Pedersen,* Linkoping University, Sweden

The properties of aluminum nitride (AlN), including a wide bandgap (6.2 eV), high dielectric constant ($k \sim 9$), high electrical resistivity ($\rho \sim 10^{11}–10^{13}$ Ω cm), and high thermal conductivity (2.85 W/K cm)[1] make it one of the commonly used materials in microelectronics and optoelectronics. AlN is also used in microelectromechanical systems (MEMS devices) due to its piezoelectric properties. It also presents good miscibility with other nitrides and can be used in ternary materials when combined with Ga, In, Ti and Hf, which increases the range of its potential applications.

Although ALD of AlN from AlMe₃ (TMA) has been widely reported to date, the surface chemistry of AlN ALD from other precursors, particularly Al(NMe₂)₃ (TDMAA) have not yet been reported. We compared AlN ALD with TMA and TDMAA as Al precursors and NH₃ with and without plasma activation as the N precursor in the temperature range from 100 to 400 °C. Using mass spectrometry, we find that the surface chemistry of the TMA-process involves reductive elimination and ligand exchange from the gaseous CH₄ detected both during the TMA- and NH₃ pulses. The TDMAA-process also involves transamination mechanisms from the N(Me)₂ and HN(Me)₂, and CH₄ detected during the NH₃ pulses.

By comparing our experimental results to modeling results[2] drawn from density functional theory methods, we can deduce a detailed, atomistic surface chemical mechanism of TMA on an NH₂-terminated AlN surface. No literature is available for theoretical studies of AlN ALD from TDMAA, making our surface chemical mechanism for the TDMAA-process less detailed.

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4:30pm **AF2-WeA-13 Investigating Hf Oxide Growth with Ambient Pressure XPS and Ozone as Co-Reactant**, *Esko Kokkonen,* Max IV Laboratory, Sweden*; R. Jones,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; C. Eads, A. Klyushin,* Max IV Laboratory, Sweden*; J. Schnadt,* Lund University, Sweden

Hafnium oxide is a promising material to be used in many applications such as high-k dielectrics or in advanced metal-oxide-semiconductor devices. The accurate knowledge of the deposition is crucial for creating pure, defect free, interfaces as well as optimising the reaction process timing and decreasing material consumption. In the past few years, ambient pressure X-ray photoelectron spectroscopy (APXPS) [1] has been used to study the ALD of HfOx on various surfaces [2,3]. These studies have focused on revealing intricate details within the first few half-cycles and have discovered new surface species, inter- and intramolecular reactions, and bimolecular reaction pathways.

The previous APXPS studies have used water as the co-reactant, but in this work, we turn our focus to ozone. We show how the experimental APXPS setup was modified to incorporate an ozone generator, and the results from the XPS analysis. The measurements were conducted in such a way that we were able to separate the contributions from oxygen and ozone to the growth in the co-reactant half-cycle.

The data indicates that oxygen alone creates very strong changes on the surface and contributes to the growth of the layers removing some ligands from the Hf precursor. Each co-reactant pulse was initiated in pure oxygen and the ozone was only started after a short delay. Deposition temperature was varied in a large range which shows strong affects on the reaction mechanism of the first few half-cycles. The study shows the importance of in situ experiments and separating the process into its constituent components in order to understand them better.

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4:45pm **AF2-WeA-14 ALD/ALE 2024 Closing Remarks**, *Mikko Ritala*, M. Leskelä, University of Helsinki, Finland*; F. Roozeboom,* University of Twente and Carbyon B.V., The Netherlands*; D. Suyatin,* AlixLabs A.B., Sweden

ALD Fundamentals
Room Hall 3F - Session AF3-WeA

Growth and Characterization: Plasma Enhanced ALD II

Moderators: **Matti Putkonen**, University of Helsinki, **Mikko Söderlund,**, Beneq Oy

4:00pm **AF3-WeA-11 UHP PEALD Growth and High Field Dielectric Testing of κ-Ga₂O₃ Films**, *Bangzhi Liu,* The Pennsylvania State University

[1]Bangzhi Liu, [1]Yeseul Choi, [1]Smitha Shetty, [2]Gilbert B. Rayner, [1]Fan He, [3]Kunyao Jiang, [1]Benjamin L. Aronson, [3]Jingyu Tang, [4]Yongtao Liu, [4]Kyle P. Kelley, [3,5]Jr.; Robert F. Davis, [3]Lisa M. Porter, [1,6]Susan Trolier-McKinstry

1. Materials Research Institute, Penn State University; 2. The Kurt J. Lesker Company; 3. Materials Science and Engineering, Carnegie Mellon University; 4. Oak Ridge National Laboratory; 5. Electrical and Computer Engineering, Carnegie Mellon University; 6. Materials Science and Engineering, Penn State University

Ga_2O_3 has multiple different polymorphs: α-, β-, γ-, and ε(κ)-phases. β-Ga_2O_3 has drawn significant attention in the power electronics community since it is an ultra-wide bandgap semiconductor and, fortunately, the only thermodynamically stable phase. The ε (also called κ)-phase is the next most stable polymorph. This metastable phase has been predicted to be ferroelectric[1,2] and can be a suitable candidate for non-volatile memory applications if its ferroelectricity is confirmed. Technically, using ALD to grow this film is ideal for memory device fabrication, given its precise thickness control and excellent conformality.

To this end, we invested significant effort in developing a Plasma-Enhanced ALD (PEALD) process to grow κ-phase with c-orientation on a conductive substrate for electrical testing. The deposition system used was a KJ Lesker ALD150LX operating under ultrahigh purity (UHP) conditions. A major challenge was to find conditions that favor the formation of metastable κ-phase while suppressing the growth of stable β-phase. By controlling O_2 flow, vacuum level, plasma power, growth temperature and substrate type, we successfully grew c-oriented κ-phase (50 nm thick) on platinized sapphire substrates. The films were characterized by ellipsometry, FESEM, XRD, and ToF SIMS for material properties and by high field dielectric testing and Piezoresponse force microscopy for the possible ferroelectric properties. A comparison was made to Metal-Organic Chemical Vapor Deposition (MOCVD) grown thick films (700 nm) with predominantly the κ-phase prepared by our collaborators in parallel to better evaluate the ferroelectricity of κ-Ga_2O_3[3].

4:15pm AF3-WeA-12 Crystalline Phase Control of Manganese Oxide Films by Plasma Enhanced Atomic Layer Deposition, *Zhongwei Liu, J. Ren, H. Fang, L. Sang,* Beijing Institute of Graphic Communication, China

Over the past decades, manganese oxides have attracted increasing interests due to their various compositions, such as MnO, Mn2O3, MnO2, Mn3O4, and Mn5O8, in which several oxidation states, +2, +3, and +4 exist. The multitude of structures and valence state offer a number of applications for manganese oxides in catalysis, microelectronic, biosensors, and Li ion battery. In this work, we developed a plasma enhanced pulsed chemical vapor deposition process for manganese oxide (MnOx) thin films using bis(1,4-di-tert-butyl-1,3-diazabutadienyl)manganese(II) (Mn(dad)2) as the Mn precursor. Mn(dad)2 is an active compound with high volatility, and suitable for CVD or ALD process. MnOx film was characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) (FEI Talos F200S). The effects of the deposition temperature and the types gases, such as H2, Ar, H2 plasma and Ar plasma, on phase composition of manganese oxides were carefully investigated. When Ar or H2 gas was employed as the discharge gas and the deposition temperature was 120 ℃, amorphous or nanocrystalline MnOx was obtained. In contrast, the film grown in Ar plasma was a face-centered cubic (fcc) MnO structure. In the case of H2 plasma, the diffraction peaks can also be indexed to fcc MnO, except that the preferred orientation of the film was different. As the deposition temperature was increased to 180 ℃, the film deposited in Ar or H2 gas showed Mn3O4 structure. Similar to that grown at 120 ℃, the film deposited at 180 ℃ in Ar or H2 plasma was identified to be MnO, indicating that the deposition temperature has negligible effect on the film crystallinity under plasma condition. If the deposition temperature was further raised to 240 ℃, a mixture MnO and Mn3O4 was obtained for the films grown in Ar or H2 gas, while in the case of Ar or H2 plasma, the afforded film is still MnO. These results indicated that the plasma had a significant effect on MOx crystalline phase.

4:30pm AF3-WeA-13 Superconducting Ultrathin Niobium Nitride Films for Quantum Application, *Mario Ziegler, E. Knehr, E. Mutsenik, S. Linzen, G. Oeslner, E. Il'Ichev, R. Stolz,* Leibniz Inst. of Photonic Technology, Germany

Superconducting thin films are the basis for a wide range of applications such as quantum cryptography, sensing, quantum metrology or quantum computing. On one hand, devices such as superconducting nanowire single photon detectors (SNSPDs) are in need for high-quality films with high critical temperatures (Tc) [1]. Especially in transition from single- to multi-pixel devices, the properties have to be uniform over a large surface area. On the other hand, novel concepts of second generation quantum devices such as charge quantum interference devices based on coherent quantum phase slip require disordered superconductors with high kinetic inductance [2,3]. NbN is a promising candidate as the Tc (bulk T_C=16\ K) in comparison to TiN, TaN, MoSi or WSi allows for higher operating temperatures, higher switching currents, and thus a better signal-to-noise ratio. Nevertheless, the variety of applications demands for a flexible and adaptable manufacturing process with very good control of the thin-film properties, ideally over a larger surface area.

In this context, plasma-enhanced atomic layer deposition (PE-ALD) exhibits very good thickness homogeneity over a broad surface area as well as a nearly perfect thickness control. But when it comes to quantum applications, homogeneity is not only determined by roughness and layer thickness. Also, electrical properties such as normal sheet resistance, critical temperature, or critical current density must be considered. Up to now, PE-ALD processed NbN achieved Tc of 14 K for a 21 nm thick film [4] and even films with 2.7 nm thickness are still superconductive [2]. NbN films made by PE-ALD revealed a complex chemical composition not only consisting of stoichiometric NbN but also of niobium carbide, niobium oxide, and niobium-oxynitride. We observed that the electrical properties changed drastically, whereas film thickness and roughness remained almost constant. The deviations might originate from the reactor geometry or fluctuations of precursor supply during the deposition process. We will present optimized fabrication recipes for SNSPDs with high Tc as well as for circuits of highly disordered superconducting materials [2,3,5].

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Atomic Layer Etching
Room Hall 3F - Session ALE-WeA

Modeling in Atomic Layer Etching
Moderators: Steven M. George, University of Colorado at Boulder, **Dmitry Suyatin**, AlixLabs A.B.

1:45pm ALE-WeA-2 Utilizing Thermodynamic Analysis to Screen Material and Precursor Selection for Selective Thermal Atomic Layer Etching, *Landon Keller,* North Carolina State University*; M. McBriarty, B. Zope, M. Moinpour, R. Kanjolia,* Merck KGaA, Darmstadt, Germany*; G. Parsons,* North Carolina State University

Advanced patterning of microelectronic devices requires better understanding and control of chemical mechanisms during atomic scale processing for fabrication of advanced architectures. Thermal atomic layer etching (ALE) is a promising approach to achieve controlled etching and chemical selectivity, but it is not yet widely used in semiconductor manufacturing. To advance ALE, new precursor systems must be identified and discovered to create new viable processed for use in backend applications. In this work, we report a methodology for screening material-precursor systems to be used in ALE using tabulated thermodynamic properties of condensed and gaseous compounds.

Previously, our group developed an ALE process for etching TiO_2 ALD films using WF_6/BCl_3.[1] Using our learning from this process, we performed thermodynamic analysis of Gibbs free energy values and equilibrium compositions using a software package called HSC Chemistry 10.[2] The HSC software generates equilibrium composition diagrams and predicts reactions products in a closed system that can be analyzed through an iterative approach to predict process conditions where reactions should occur thermodynamically and identify conditions for ALE or continuous vapor etch (CVE) across a temperature range. Figure 1a shows that after exposure of TiO_2 to WF_6, solid surface products $TiF_4(s)$ and $WO_3(s)$ are predicted to form from 50°C-195°C. TiO_2 was also exposed to BCl_3 and solid $B_2O_3(s)$ is expected to form across the entire temperature range, as shown

in Figure 2b. To mimic an ALE process, the solids formed in Figure 1a were exposed individually to BCl_3 and results are shown in Figures 1c-1d. Solid conversion layers generated on the surface after BCl_3 exposure were next exposed to WF_6 to represent a 2nd ALE cycle. Solid products $WO_2Cl_2(s)$ and $B_2O_3(s)$ were predicted to form and the resulting products after exposure to $WF_6(g)$ are shown in Figures 1e-1f. Figures 1a-1b predict CVE of TiO_2 to occur using WF_6 and not BCl_3 over the temperature range 195°C-400°C. When all the equilibrium species are analyzed together, ALE of TiO_2 is predicted to be possible from 155°C-195°C, with no etching occurring below 155°C. This methodology was repeated with 3 other material systems and their predicted CVE and ALE temperature ranges are shown in Table 1. These results can be compared with experimental data to assess the validity of the predicted temperature ranges.

We believe these findings provide a reliable methodology to predict material-precursor systems for CVE and ALE and will aid with the discovery of new etch systems for atomic scale processing within semiconductor manufacturing.

2:00pm ALE-WeA-3 Atomistic Surface Processing Simulations: ALE of Transition Metal Dichalcogenides, *Suresh Kondati Natarajan, N. Pandey, J. Schneider, J. Wellendorff,* Synopsys Denmark ApS, Denmark

Atomic Layer Etching (ALE) is becoming a key thin-film processing technique to enable next-generation semiconductor technology nodes. As ALE employs cyclic processing of materials using sequential self-limiting surface reactions, it can be used in conjunction with atomic layer deposition (ALD) to prepare conformal and smooth nanoscale patterns of extreme limits in semiconductor device fabrication. One of the upcoming ALE applications is preparing CMOS channels based on novel transition metal dichalcogenide (TMD) materials, such as MoS_2, WS_2, $MoSe_2$, and others, which may in time replace silicon. TMDs consist of three atomic planes forming a single layer, and the process to etch TMDs must ensure the removal of the three atomic planes conformally to avoid impurities [1]. The layer-by-layer etching process of TMDs therefore needs special considerations to ensure high conformality, avoid over/under etching of TMD layers, and at the same time provide maximum process capability and yield. In the process of adding or removing surface material atom-by-atom, in-silico atomic-scale modeling approaches are key to understanding mechanisms, finding optimal energies of the reacting species for maximum yield, and predicting process outcomes. Synopsys has developed an industry-grade simulation framework within the Synopsys QuantumATK software [2,3] for atomistic surface processing and have previously demonstrated it for ALD of HfO_2 [4].

In this talk, we will present enhancements of this simulation workflow to simulate ALE processing of TMDs (specifically MoS_2), using sequential Cl_2 plasma exposure and Ar ion bombardment [1]. The simulation workflow involves molecular dynamics simulations with specifically trained machine-learned force fields (ML FFs) and can in principle be applicable to ALE processing of any material.

We will first discuss the simulated saturation profiles of Cl uptake during the Cl_2 plasma pulse along with the trend in the dissociative sticking probability/coverage of Cl_2 molecules as a function of its impact energy. Following that, we will showcase the results for the etch rate during cyclic exposure of Cl_2 plasma and Ar ion along with a list of possible etch by-products. Finally, we will discuss the effect of Ar impact energy and impact angle on the etch rate (yield) at saturated Cl coverage.

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2:15pm ALE-WeA-4 Gas-Phase Etching Mechanism of Amorphous Hydrogenated Silicon Nitride by Hydrogen Fluoride: A Theoretical Study, *Khabib Khumaini, Y. Kim, R. Hidayat, T. Chowdhury, H. Kim,* Sejong University, Republic of Korea*; B. Cho, S. Park,* Wonik IPS, Republic of Korea*; W. Lee,* Sejong University, Republic of Korea

Understanding the etching reaction mechanism is essential for the design and optimization of the etching process. However, the theoretical study of the etching mechanism is challenging due to the significant influence of crystallinity and impurities. Gas-phase etching of silicon nitride using hydrogen fluoride (HF) vapor provides an alternative to wet etching, particularly for addressing pattern-leaning issues in nanoscale structures. The etching process is continuous at elevated temperatures but exhibits self-limiting behavior at low temperatures [1]. Nevertheless, the atomic-scale mechanism remains poorly understood. Therefore, we performed density functional theory (DFT) calculations to study the etching mechanism [2]. Since silicon nitride films are typically amorphous with significant hydrogen impurities, we created an amorphous substrate model with a hydrogen concentration of 25 at.%. We then constructed four different slab models representing different degrees of fluorination and simulated fluorination pathways. All of the fluorination reactions were exothermic, but the activation energies varied. The cleavage of Si–N or Si–Si bonds and the release of byproducts showed low activation energies, indicating that etching would be plausible. We also simulated the formation and desorption of the $(NH_4)_2SiF_6$ salt on the fluorinated surface. The salt formation was also favorable due to low activation energies, which explains the self-limiting behavior of silicon nitride etching at low temperatures. However, at 152°C or higher, $(NH_4)_2SiF_6$ would decompose into gaseous byproducts, which explains the high etch rate at elevated temperatures. Our DFT calculation using the hydrogenated amorphous silicon nitride slab model successfully explained the etching of silicon nitride films by HF, which a crystalline Si_3N_4 slab model could not explain. Therefore, a slab model with the same composition and structure as the thin film to be etched is required to simulate the etching process.

References [1] G. Vereecke and M. Meuris, EP1083592A1 (14 March 2001) [2] K. Khumaini et al., Appl. Surf. Sci. 654 (2017) 159414.

2:30pm ALE-WeA-5 Dynamic Global Model of Cl_2/Ar Plasmas for Atomic Layer Etching of GaN, *Tojo RASOANARIVO, C. Mannequin,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean ROUXEL, France*; F. ROQUETA, M. BOUFNICHEL,* STMicroelectronics, France*; A. RHALLABI,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean ROUXEL, France

Plasma Atomic Layer Etching (ALE) is an etching cyclic process. One ideal ALE cycle consists of two self-limited half reactions, separated by purge: an adsorption step to modify the uttermost surface layer and an activation step to selectively remove the modified layer without etching the underneath non-modified layers with an atomic scale resolution. ALE of GaN by alternating Cl_2 and Ar plasma, for the adsorption and activation steps, respectively, has been extensively studied [1]. In these processes, adsorption step is believed to rely on surface modification by chlorine radicals while activation is achieved by selectively controlling the energy of an ionic bombardment. However, these studies mostly focus on experimental approaches and modelling investigations are scarce.

As ALE is atomically sensitive, to better understand plasma/surface interactions at atomic scale, we must first precisely investigate plasma dynamics during the change from Cl_2 to Ar plasma corresponding to the transition from the adsorption to activation step. To date, global models have been well implemented to determine the plasma composition at specific plasma reactor parameters, with good computational time effectiveness [2]. These global models were initially designed to describe plasmas in steady-state conditions [3] and without considering any time dependent variations of the feedgas.

In this work, we develop a dynamic global model for Cl_2/Ar plasmas that follows time evolution of the plasma over a complete ALE cycle by modelling feedgas switches and RF power variations. Our model allows the calculation of neutrals and ions densities evolution over time, especially during the dynamic feedgas switch from a Cl_2 to an Ar plasma. We investigate the effects of the operating conditions such as RF power, pressure and total feedgas flowrate on the evolution of species densities and electron temperature. Higher chlorine species densities can be attained during the Cl_2 to Ar transition compared with a pure Cl_2 plasma. Long residence times for Cl_x species open the question on how to precisely control the surface reactions in GaN ALE.

Références

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2:45pm ALE-WeA-6 A Transient Surface Site Balance Model for Si-Cl2-Ar Atomic Layer Etching, *J. Vella,* Princeton Plasma Physics Laboratory*; David Graves*, Department of Chemical and Biological Engineering Princeton University and Princeton Plasma Physics Laboratory **INVITED**

Plasma-assisted atomic-layer etching (ALE) processes have the potential to attain controlled substrate removal.[1] While ALE is used in industry, there is still a lack of fundamental understanding surrounding many aspects of the processes. Simulation and modeling can help fill knowledge gaps, which will lead to the development of more efficient ALE processes. Previously, we have focused on modeling Si-Cl2-Ar ALE using molecular dynamics (MD) simulations, which have been validated against experiments.[2-4] We use the results from the MD simulations to develop a transient surface site balance model inspired by the work of Gray et al.[5] and Chang et al.[6] Within the model, the Si substrate is divided into three regions: the top, the mixed, and the crystalline layers. The model considers both the chlorination (surface modification) and ion bombardment (removal) sub-steps. The model accounts for Si and Cl present in the top and mixed layers of the substrate and thus all etched and sputtered products. Mixing of Cl from the top layer into the underlying mixed layer is also modeled. It is shown that this model accurately reproduces MD and select experimental results. The transient site balance model provides an intuitive methodology for modeling ALE processes and can be generalized to more complex processes and materials.References[1] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, "Overview of Atomic Layer Etching in the Semiconductor Industry", J. Vac. Sci. Technol. A, 2015, 33, 020802.[2] J. R. Vella, D. Humbird, and D. B. Graves, "Molecular Dynamics Study of Silicon Atomic Layer Etching by Chlorine Gas and Argon Ions", J. Vac. Sci. Technol. B, 2022, 40, 023205.[3] J. R. Vella and D. B. Graves, "Near-Surface Damage. And Mixing in Si-Cl2-Ar Atomic Layer Etching Processes: Insights from Molecular Dynamics Simulations", J. Vac. Sci. Technol. A, 2023, 41, 042601.[4] J. R. Vella, Q. Hao, V. M. Donnelly, and D. B. Graves, "Dynamics of Plasma Atomic Layer Etching: Molecular Dynamics Simulations and Optical Emission Spectroscopy", J. Vac. Sci. Technol. A, 2023, 41, 062602.[5] D. C. Gray, I. Tepermeister, and H. H. Sawin, "Phenomenological Modeling of Ion-Enhanced Surface Kinetics in Fluorine-Based Plasma Etching", J. Vac. Sci. Technol. B, 1993, 11, 1243-1257.[6] J. P. Chang, J. C. Arnold, G. C. H. Zau, H. Shin, and H. H. Sawin, "Kinetic Study of Low Energy Argon Ion-Enhanced Plasma Etching of Polysilicon with Atomic/Molecular Chlorine", J. Vac. Sci. Technol. A, 1997, 15, 1853-1863.

3:15pm ALE-WeA-8 Theoretical Analysis on Halogenation of Transition Metal Surfaces toward Thermal Atomic Layer Etching, *Hyun Cho, M. Kim, B. Shong,* Hongik University, Republic of Korea

In fabrication of the semiconductor devices involving three-dimensional structures with shrinking sizes, challenges in etching processes are being emphasized, such as roughness and selectivity issues. Atomic layer etching (ALE) is a possible alternative etching technology that removes small designated amount of material per process step in a self-limiting manner, resulting in precise control over the etch thickness and reduced roughness. Especially, in order to enable isotropic etch processes at the inner surfaces of three-dimensional substrates, thermal ALE processes comprised entirely of reactions of neutral reactant molecules are desirable. Many recent reports on thermal ALE utilize halogenation reaction at either conversion or volatilization steps. Since such surface reactions strongly depend on the substrate materials and halogenation reactants, it is desirable to identify the reactivity of possible self-limiting halogenation according to the reactant-substrate combinations. In this study, we conducted an analysis on the energetics of the surface halogenation of some transition metal surfaces, using density functional theory (DFT) and machine learning potential (MLP) calculations. By calculating the adsorption energy of Cl and F atoms depending on their surface coverage, as well as the energy change in conversion into metal halide overlayers, the spontaneity according to the degree of halogenation could be compared. The different reactivities of several molecular chlorination and fluorination agents, such as Cl_2, F_2, $SOCl_2$, and SF_4, are also compared.

Acknowledgments. This work was supported by Samsung Electronics.

Emerging Materials
Room Hall 3E - Session EM-WeA

Other Emerging Materials

Moderators: **Jiyoung Kim**, University of Texas at Dallas, **Mato Knez**, CIC nanoGUNE

1:30pm EM-WeA-1 Atomic-Scale Homogeneous PtRu Alloy Thin Films Prepared by Atomic Layer Modulation (ALM), *Yeseul Son, S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; T. Cheon,* Daegu Gyeongbuk Institute of Science and Technology, Republic of Korea*; S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea

To create multi-component thin films with ALD, the super-cycle method is commonly used. By adjusting the cycle for each ALD process of each material to be mixed at an appropriate ratio, it is possible to produce a thin film with an arbitrary element ratio. However, the distribution of elements in the depth (thickness) direction is non-uniform or forming nano-laminate structure, and to obtain the composition of the desired ratio, it is necessary to produce a thin film of at least several nm. In this study, to address this problem, a newly proposed atomic layer modulation technology (ALM) [1] was used. ALM technology enables the production of uniform multi-component thin films at the atomic layer level by sequentially exposing multiple precursors within one cycle [Fig. 1]. So, atomic-scale homogeneous alloy films of Pt, which is highly active in hydrogenation reactions and has a bulk resistivity of 10.6 μΩ cm and work function of 4.71 eV, and Ru, which is highly active in oxygenation reactions and has a bulk resistivity of 7.1 μΩ cm and work function of 5.65 eV, was successfully prepared [Fig. 2]. Here, metal-organic precursors, tricarbonyl(trimethylenemethane)ruthenium $[Ru(TMM)(CO)_3]$ and dimethyl-(N,N-dimethyl-3-butene-1-amine-N)platinum $(C_8H_{19}NPt)$ were used and a self-limiting growth for each Ru and Pt ALD, was confirmed. By controlling the condition of ALM process, we can prepare ALM PtRu alloy thin films with different compositions and their properties with the composition were systematically analyzed by SIMS, TEM, XPS, XRD, XRR etc. The performance of ALM PtRu alloy film as a wiring material to replace Cu as well as a catalyst for HER (hydrogen evolution reaction) and OER (oxygen evolution reaction) will be presented in the conference.

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[1] Nguyen, C. T., et al., "Atomic Layer Modulation of Multicomponent Thin Films through Combination of Experimental and Theoretical Approaches", Chem. Mater. 2021, 33, 4435−4444.

1:45pm EM-WeA-2 A New Approach to the Synthesis of Nb@TiO₂ Core-Shell Composite for Oxide Dispersion Strengthened Alloy via Atomic Layer Deposition, *Ji Young Park, E. Lee, M. Jeong, J. Byun, B. Hwang, S. Oh, B. Choi,* Seoul National University of Science and Technology, Republic of Korea

More than half of CO_2 emissions in the world come from fossil fuels; therefore, in order to significantly reduce them, it is necessary to develop efficient internal combustion engines. In an attempt to enhance their mechanical properties in extreme conditions, it is required to have high thermal stability and strength as well as high durability and corrosive resistance. Nowadays, many types of research (alloying, surface and heat treatments, etc.) have been conducted to develop eligible refractory materials.

Nano-oxide dispersion strengthened (ODS) refractory alloy has been attracting attention because of its outstanding mechanical reinforcement mechanism. Dispersed oxides enhance the strength by preventing grain growth and recrystallization as well as increasing creep resistance, which allows ODS to be widely applied in extreme fields such as military industries and aerospace. ODS alloys are commonly fabricated by mechanical alloying methods. However, it can draw impurities and cracks in raw powders, which influence on porosity of pellets. In this research, atomic layer deposition (ALD) is applied to synthesize ODS alloy. ALD is one of the most promising technologies in thin film deposition. It is useful to coat conformal thin films even on complex shapes of matrix such as nanorods or powders without mechanical damage. We coat pure Nb powder with TiO_2 thin film by using rotary-reactor type thermal ALD. TiO_2 chosen as the coating layer is non-toxic and chemically stable in high temperatures. In addition, it has superior mechanical strength as well as anti-wear and corrosion properties, thus widely adopted to ODS. TiO_2 is grown by using Titanium tetraisopropoxide (TTIP) precursor and H_2O reactant gas at 200°C. Transmission electron microscopy analysis reveals that TiO_2 is deposited uniformly on the Nb powder and the thin film in pellets is dispersed to be crystallized. Spark

plasma sintering method is applied for sintering powders to minimize residual stress and grain coarsening. Thin film analysis including X-ray photoelectron spectroscopy and X-ray diffraction is conducted to understand the physical and chemical properties of the coating layer and its matrix. Grains with grain boundaries in pellets are analyzed via electron backscatter diffraction method. Mechanical properties are investigated by Vickers hardness test and nanoindentation measurement to confirm the TiO_2 dispersion strengthening effect on Nb refractory matrix. This study proposes a new field of ALD. This technology can be further applied to the surface and interface engineering of powder materials for electronic and energy applications.

2:00pm EM-WeA-3 Influence of an Artificial Structure on the Mechanical Properties of Atomic Layer Deposited Al_2O_3 and Ta_2O_5 Composite Thin Films, *Helle-Mai Piirsoo, T. Jõgiaas, K. Kukli,* University of Tartu, Estonia
The functionality of nanodevices depends on the mechanical reliability of their components like thin films. It has been shown that atomic layer deposited oxides in a periodic layered architecture possess lower residual tensile stresses [1], higher hardness [2], better wear properties [3] compared to their single constituents. ALD-grown nanocomposite thin films can improve the mechanical resistance of nanodevices.

In this work, amorphous Al_2O_3 and Ta_2O_5 thin films, their nanolaminates and mixtures were atomic layer deposited to thicknesses of ~70 nm. The single constituent layer thickness in multilayers, consisting of equal amounts of Al_2O_3 and Ta_2O_5, was varied from 18 to 1 nm. Trilayers with varying oxide volume fractions were deposited. The films were annealed at 800 ºC for 10 min in air.

The amorphous reference Al_2O_3 film was harder compared to reference Ta_2O_5 by ~3 GPa and possessed ~15 GPa higher Young's modulus [4]. The hardness did not vary with the single layer thickness of amorphous nanolaminates, while mixtures were slightly harder compared to the laminates (Fig. 1). The elastic modulus decreased below that of the references in some multilayers (Fig. 2).

Annealing promoted the formation of orthorhombic Ta_2O_5 phase in the reference film [5] and in some composites. The Al_2O_3 film remained amorphous. The single constituent layer thickness had an influence on the hardness in nanolaminates with crystallized Ta_2O_5 layers. Nanolaminates with constituent layer thickness below 12 nm remained X-ray amorphous and softer compared to the crystalline nanolaminates and mixtures (Fig.1). The elastic modulus was modified with annealing for some of the multilayers (Fig.2).

The architecture of the trilayers affected hardness more than the Al_2O_3/Ta_2O_5 volume ratio, while the modulus of elasticity increased with increasing Al_2O_3 content after annealing.

The results show a possibility of engineering the mechanical properties of ALD thin films.

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2:15pm EM-WeA-4 ALD Young Investigator Award Finalist Talk: Phosphorus-Rich Metal Phosphide Thin Films Using Zintl Ions, *Jordan Bentley,* University of Western Ontario, Canada; *B. van Ijzendoorn,* Manchester Metropolitan University, UK; *J. Lomax,* University of Western Ontario, Canada; *M. Bakiro, S. Barry,* Carleton University, Canada; *M. Mehta,* Manchester Metropolitan University, UK; *P. Ragogna,* University of Western Ontario, Canada
Metal phosphide thin films can be prepared by vapour deposition techniques using various metal and phosphorus precursor combinations.[1] The resulting materials have applications in microelectronics, catalysis, and energy storage. For example, transition metal analogues such as FeP, CoP, and NiP, are effective catalysts in hydrogen evolution reactions or as electrode materials for Li-ion batteries.[2,3] As for main-group metals, group 13 and 14 congeners such as GaP, InP, and GeP possess bandgaps that are amenable to photovoltaic and transistor applications.[4] Metal phosphides usually require organophosphorus or PH_3 as the phosphorus source, but here, we demonstrate that the heptaphosphide cluster (P_7^{3-}) can serve as an effective phosphorus precursor for making thin films by molecular layer deposition.[5] This opens a pathway to phosphorus-rich metal phosphide thin films (MP_2, MP_3, MP_4) which can exhibit superior properties to binary metal phosphides in some cases.[6] We used a specially designed crossflow vapour deposition system and then annealed the films to achieve uniformity. To the best of our knowledge, this is the first time that main group clusters were employed in vapour deposition. This opens up the possibility of creating novel materials with tailored properties at the nanoscale level. Current data supports that $P_7(SiMe_3)_3$ is sufficiently robust up to ~250 ºC as measured by DSC and can be volatilized. A volatilization temperature under 1 torr (T_v) was estimated to be ~130 ºC; isothermal data at 130 ºC and 150 ºC support the linear mass loss of $P_7(SiMe_3)_3$ over 2 hours. We will present details on the precursor, thin film preparation, and analyses such as powder X-ray diffraction, electron dispersive spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and quartz crystal microbalance.

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2:30pm EM-WeA-5 Improved Crystallinity and Polarity Determination of Gallium Nitride on Si (111) Using Atomic Layer Annealing, *S. Yun, **Ping-Che Lee**,* University of California San Diego; *A. Mcleod,* University of California at San Diego; *J. Spiegelman,* RASIRC; *A. Kummel,* University of California at San Diego
The crystallinity and polarity of III-V semiconductors are critical for the passivation layers on microLED, the formation of 2D electron gasses in high electron mobility transistors, and for templating growth of piezoelectric materials. The atomic layer annealing (ALA) was reported to improve the crystallinity of the III-V compounds (aluminum nitride) at low temperatures as compared to the conventional thermal ALD. In ALA, a pulse of ion bombardment is added to each ALD cycle to ensure polycrystalline film formation at low temperature. Polycrystalline GaN has been deposited by ALA at low temperatures even on amorphous substrates, but polarity was not reported.

Figure 1a and 1b show the process parameter switching diagram for the GaN thermal ALD and GaN ALA processes, respectively. For GaN, tris(dimethylamido)gallium(III) (Strem Chemicals) and N_2H_4 (Rasirc) were used as precursors. The chemical compositions of GaN ALDs/Si were estimated by *in-situ* AES as shown in Figure 1c. Lower O contents (below 3.3 at. %) and higher N/Ga atomic ratio were observed in the ALA GaN on Si (111) as compared to the thermal ALD GaN film (4.6 at. %). Figure 1d shows that the intensity of GaN (002) XRD pattern in thermal ALD GaN on Si was greatly improved in the GaN stacks (GaN thermal ALD/ALA/Si) with an ALA GaN buffer layer.

Figure 2a and 2b shows the HAADF-STEM images of GaN ALDs/Si demonstrate highly ordered 3 nm × 5 nm ALD GaN layers. The circles of bright regions and the center of dark regions represent Ga atoms and tunnel points (empty element), respectively. The GaN polarity could be determined by drawing triangles connecting adjacent three tunnel points without the interruption of Ga. Using this method, upward triangles were obtained in the Figure 2a, suggesting the formation of N-polar GaN layers during the ALA GaN process on Si. Conversely, downward triangles from the STEM image of thermal ALD GaN/ALA/Si (Figure 2b) suggested Ga-polar GaN during GaN thermal ALD process. The inset figures show the top-view SEM image of selectively wet-etched (30 min, 20 wt.% KOH(aq)) GaN films. The etched surface on the ALA GaN (inset of Figure 2a) indicated N-polar GaN surface. The inset SEM image in Figure 2b shows a nearly unchanged GaN surface in thermal ALD GaN/ALA/Si is consistent with the Ga-polar GaN surface. These observations are in good agreement with the HAADF-STEM images.

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The data is consistent with being able to control the polarity of GaN by switching between thermal ALD and ALA. The ion bombardment in ALA promotes N-polar GaN while thermal ALD promotes metal polar GaN. This allows the facile formation of both electron and hole gas layers between ALA and ALD GaN.

2:45pm EM-WeA-6 Self-limiting Epitaxy of GaN and InN Films on Sapphire Substrates, *S. Allaby, N. Ibrahimli, F. Bayansal, H. Saleh, B. Willis,* **Necmi BIYIKLI**, *University of Connecticut*

Research efforts on low-temperature (T < 300 °C) synthesis of crystalline III-Nitride thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to oxide-free stainless-steel based hollow-cathode plasma (HCP) sources revealed highly (002) oriented polycrystalline GaN films on Si(100) and sapphire substrates. In this work, we share our experimental findings on the self-limiting growth of GaN and InN films on sapphire substrates using HCP-ALD at 200 °C substrate temperature, revealing (002) oriented hexagonal monocrystalline layers.

The films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and various nitrogen plasmas (N_2/H_2, N_2-only, N_2/Ar, and $N_2/H_2/Ar$) as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed at 200 °C substrate temperature and a mild 100 W rf-power. *In-situ* Ar-plasma annealing cycles were also employed and tested for the binary III-nitride films to observe its impact on the surface crystallization process. *In-situ* ellipsometry was employed to monitor the surface ligand-exchange reactions and plasma surface interactions, in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness variation, growth-per-cycle (GPC), and optical properties of the III-nitride films.

When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for III-nitride films on c-plane sapphire substrates showed a notable increase. Grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline GaN and InN films on Si(100) substrates while GaN/sapphire and InN/sapphire film samples exhibited substantially weaker crystal peaks or no peaks at all. XRD ($\theta - 2\theta$) scans displayed strong (002) peaks for both nitride films grown on sapphire substrates, confirming the monocrystalline epitaxial character of the synthesized GaN/sapphire and InN/sapphire samples. The impact of plasma gas mixture and Ar-plasma annealing process revealed different results for GaN versus InN films. While H_2-containing plasmas are optimal for GaN, InN prefers H_2-free plasma gas mixtures. Also, Ar-plasma annealing improved GaN film properties while degrading InN film quality.

3:00pm EM-WeA-7 Epitaxial Rare-Earth Orthoferrites by Atomic Layer Deposition, *Linn Rykkje, H. Sønsteby, O. Nilsen,* University of Oslo, Norway

Rare earth orthoferrites ($RFeO_3$, R = lanthanide) are a class of materials whose optical and multiferroic properties demonstrate a rich landscape of functionalities. While their ferroelectric and -magnetic behavior are interesting in themselves, it is the potential for magnetoelectrically coupled behavior that make them fascinating candidates for applications in photoferroics [1][2], photocathodes [3], spintronics [4][5], gas sensing [6], and memory storage [1], among others.

The number of studies on orthoferrites has seen a rise in tandem with a growing awareness of their potential, but much of their fundamental behavior remains to be elucidated. Compared to more renowned multiferroics, like $BiFeO_3$, the rare earth orthoferrites are practically unexplored, despite exhibiting very similar characteristics.

A particularly interesting member to study is $NdFeO_3$, which, based on first principles calculations, is located near a multiphase boundary and could exhibit a giant polarization in a phase reminiscent of $BiFeO_3$[7][8].

To achieve such giant polarization, it would be necessary to impose significant compressive strain or apply chemical pressure (through the choice of rare earth) - both of which are highly compatible with the control leveraged by ALD as shown in our previous work. A second pathway towards functionalization is via A- or B-site substitution – which is also attainable by ALD.

The work presented here demonstrates a viable ALD synthesis route for $NdFeO_3$ thin films with tunable chemical composition and crystallinity achieved after annealing. The growth of the binary oxide layers (Nd_2O_3 and Fe_2O_3) on surfaces terminated by each other has been thoroughly investigated using quart crystal microbalance (QCM) and found to differ significantly. This is surprising given the similarity of the cation precursors used.

While the thin films have not been electrically conductive or any polarization tested at the time of writing, we believe that our approach will shed light on the structure-property relations of an elusive group of materials that are candidates for new functionality in a range of applications. We present characteristics of the ALD-process(es), as well as initial results on structural integrity and functionality.

For references, see Supplemental Document.

3:15pm EM-WeA-8 Area Selectivity and Crystallographic Orientation of ZIF-8 Films Deposited by Molecular Layer Deposition, *Jorid Smets, V. Rubio-Giménez,* KU Leuven, Belgium*; S. Armini,* IMEC Belgium*; R. Ameloot,* KU Leuven, Belgium

Integrating metal-organic frameworks (MOFs) into microfabrication processing requires highly controlled vapor-phase deposition techniques. This study presents a vapor-phase method that enables crystallographic control and direct area-selective deposition of zeolitic imidazolate framework 8 (ZIF-8). The deposition process involves a two-step ZIF-8 molecular layer deposition (MLD), during which an amorphous precursor layer is initially deposited through consecutive self-saturating reactions of diethyl zinc, water, and 2-methylimidazole. Subsequently, a linker post-treatment step promotes crystallization. The use of substrates functionalized with self-assembled monolayers (SAMs) with different head moieties allows tuning the degree of crystalline orientation in the resulting MOF layers. Additionally, the functional groups of the SAMs influence the mobility of the ZIF-8 building blocks on the surface, enabling control over the surface coverage through area-dependent surface diffusion. By exploiting this phenomenon, we successfully achieved direct area-selective deposition of ZIF-8, which can facilitate the integration of MOFs into microelectronics.

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