Tutorial Session (ALL INVITED SESSION)
Room Live - Session TS1-SuM

ALD/ALE Tutorial Session

Moderators: Prof. Seán Barry, Carleton University, Canada, Dr. Scott Clendenning, Intel Corporation

10:00am **TS1-SuM-1 Tutorial Opening Remarks & Welcome*, Seán Barry,*** Carleton University, Canada

Welcome to the ALD/ALE 2021 Tutorials! We hope you will enjoy the Session and the Virtual Meeting this week!

10:05am **TS1-SuM-2 ALE and ALD: Two Biotopes of a Kind in Atomic-Scale Processing*, Fred Roozeboom,*** Eindhoven University of Technology, TNO-Holst Centre, Netherlands **INVITED**

The IRDS 2017 Roadmap catches the scaling challenges faced by the semiconductor industry in the upcoming decades by the overall term "3D Power Scaling". In the past scaling era superior material properties and critical dimensions nearing single-digit nanometer values could still be realized by cost-effective technology solutions. As we approach the 3rd scaling era, increased complexity and cost of device fabrication can result in decreased returns for IC manufacturers. Ever more complex device architectures that are fully integrated into vertical intra- and inter-chip concepts require extreme edge placement accuracy, layer conformality and shape fidelity in all processing steps (deposition, lithography, etching).

In state-of-the-art semiconductor processing we witness an ever-progressing hybridization of individual ALD and ALE process steps into 'dep-etch' *supercycling* modes carried out in a single flowchart and a single reactor design, thereby challenging even EUV lithography. This rapid merger finds its grass roots in the close resemblance of the two techniques in terms of cyclic sequential processing, self-limiting surface chemistry and repeated etching or removal of (sub-) monolayers of material. For both ALE and ALD these factors allow for similar process windows that depend on the substrate surface temperature or the kinetic energy of reactants.

In this tutorial more parallels of ALE will be drawn with its more mature and better understood ALD counterpart. Starting with a technical-historical review of dry and reactive ion etching, the key characteristics of ALE will be discussed: the simplest ALE process is composed of two alternating steps, *i.e.* surface modification and (quasi-)monolayer removal. Next, the classification into 1) isotropic (thermal and radical-enhanced) ALE and 2) anisotropic (directional and ion-enhanced) ALE will be treated along the role played by energetic species (radicals, ions in a plasma) in one or two steps with the ions yielding anisotropic profiles (used in FinFET logic and 3D NAND memory), and neutrals and radicals yielding isotropic profiles (used to etch horizontal nanowires in GAA-FETs). Another parallel aspect that may be discussed is the need for (maskless) material-selective processing in both ALE and ALD.

In short, we will identify the similarities and differences between the two process concepts with the aim of bringing common practical insights and recommendations.

(1) The International Roadmap for Devices and Systems: 2017: More Moore; 2017.

10:55am **TS1-SuM-12 Fundamentals of Atomic Layer Deposition: An Introduction ("ALD 101")*, Riikka Puurunen,*** Aalto University, School of Chemical Engineering, Finland **INVITED**

Atomic layer deposition (ALD) has become of global importance as a processing technology for example in semiconductor device fabrication, and its application areas are continuously expanding. The significance of ALD was highlighted e.g. by the recent (2018) Millennium Technology Prize. Tens of companies are offering ALD tools, and thousands of people are involved in ALD R&D globally. A continuous need exists to educate new people on the fundamentals of ALD.

While ALD for manufacturing may be regarded mature, as a scientific field, ALD—in the author's view—is developing. For example, understanding of the early history of ALD is evolving, related to the two independent inventions of ALD under the names Atomic Layer Epitaxy in the 1970s and Molecular Layering in the 1960s [1-4]. Also, significantly varying views exist in the field related to the description and meaningfulness of even some core ALD concepts [5].

The purpose of this invited "ALD 101" tutorial is to familiarize a newcomer with fundamentals of ALD. The presentation largely follows the organization of a recent encyclopedia chapter on ALD [6]. Surface chemistry concepts will be introduced, such as ideal ALD from repeated, separate self-terminating (saturating and irreversible) reactions; growth per cycle in ALD; various monolayer concepts relevant to ALD; typical classes of surface reaction mechanisms and saturation-determining factors; growth modes; and ways to describe growth kinetics. Concepts, where differing views exist in the field and which thus need special attention, are pointed out. Typical deviations from the presented ideality are discussed.

For continuous education, a collaborative OpenLearning website on ALD is under construction [7]. Many of the images used in this tutorial—and in Refs. 6 and 7—are available in Wikimedia Commons [8] for easy and free reuse. To contribute to collective learning of the early history of ALD, the open-science effort Virtual Project on the History of ALD [4] still welcomes new volunteer participants.

[1] E. Ahvenniemi et al., J. Vac. Sci. Technol. A 35 (2017) 010801 (2017).

[2] R.L. Puurunen, ECS Transactions 86 (6) (2018) 3-17; OA: DOI:10.1149/osf.io/exyv3

[3] G.N. Parsons et al., J. Vac. Sci. Technol. A 38 (2020) 037001.

[4] http://vph-ald.com

[5] J.R. van Ommen, R.L. Puurunen, ALD 2020, https://youtu.be/jqm_wf49WwM

[6] J.R. van Ommen, A. Goulas, R.L. Puurunen, Kirk-Othmer Encyclopedia on Chemical Technology, submitted.

[7] http://openlearning.aalto.fi, ALD

[8] https://commons.wikimedia.org/wiki/Category:Atomic_layer_deposition

11:45am **TS1-SuM-22 Let's Talk Dirty - Battling Impurities in ALD Films*, Henrik Pedersen,*** Linköping University, Sweden **INVITED**

The success of ALD stems from the self-limiting nature of ALD, allowing ALD to deposit film with perfect conformality, very high uniformity, and excellent thickness control. The self-limiting nature of ALD, in turn, stems from the formation of monolayers stable enough to survive until the next pulse of reactive species. The survival of the monolayer sets an upper temperature limit for ALD and thereby an interesting challenge for the design of precursor molecules. But it also sets a challenge for managing film impurities: unwanted atoms in the ligands of the precursors are less likely to desorb from the surface at lower temperatures, creating unwanted impurities in ALD films.

In the ALD community we are quick to highlight all the nice features of ALD, but we are, perhaps naturally, less keen to discuss all the problems associated with ALD films. Film impurities is one of these problems which we do not always talk about. It is not because we do not understand the impurities or can measure them, but perhaps, partly, because we do not fully see the severity of the problem. Impurities in ALD films affect device performance by increasing leakage currents, capacitance, and electrical resistivity, and thereby decrease endurance, reliability, and cyclability of the final device. Film impurities can also badly affect the crystallinity of the film and obstruct epitaxial film growth.

Impurities in ALD films can emanate from the precursors, the carrier gas, the ALD reactor, the substrate and post-deposition handling. In this tutorial I will discuss what can be done to battle impurities from these sources. I will also compare ALD grown films with films deposited by other techniques to try to show how well ALD is doing against its competition.

12:35pm **TS1-SuM-32 Seeing Is Believing: *In situ* Techniques for Atomic Layer Deposition (ALD) Process Development and Diagnostics*, Parag Banerjee,*** University of Central Florida **INVITED**

Atomic layer deposition (ALD) has reached manufacturing scalability in industries such as, semiconductors, energy and catalysis. It is estimated that by 2025, ALD will have a market cap of ~$3.05 billion while making inroads into new industries such as, pharmaceuticals, paint products, and optics. The success of ALD as a process platform is heartening to observe, though old challenges and new bottlenecks in ALD continue to create scientific and engineering opportunities in developing new chemistries and innovation at the hardware level. One such aspect of ALD is the concurrent development and growth of *in situ* techniques that has, 1) led to a deeper understanding of the complex surface chemistries at play during an ALD process and, 2) provided a real-time platform for flagging process deviations and excursions of established ALD processes.

The use of *in situ* techniques in ALD is as old as ALD itself. In this tutorial session, I will provide a comprehensive review of *in situ* techniques published in ALD literature. These can be classified into two categories. One, where new process chemistries are unraveled. These techniques include Fourier transform infrared spectroscopy (FTIR) and quadrupole mass spectrometry (QMS). A second class of techniques involve observing physical changes to the film, such as gravimetric changes or film thickness. These techniques include quartz crystal microbalance (QCM) and spectroscopic ellipsometry (SE). Both these classes of techniques can be applied to 1) rapidly develop and optimize new ALD processes or 2) monitor established ALD processes and detect changes to deposition characteristics over time. Every technique has its set of advantages and drawbacks and practitioners of ALD will do well to understand these constraints. How well an *in situ* technique works in a scenario depends on multiple factors including hardware flexibility, process complexity and required throughout. The tutorial session will end with some emerging *in situ* techniques that are creatively applied to understand ALD processes. The potential for machine learning and advanced data science techniques to sift through massive amounts of *in situ* data will be touched upon.

1:25pm **TS1-SuM-42 ALD Powder Manufacturing***, **Arrelaine Dameron,*** Forge Nano **INVITED**

Atomic Layer Deposition (ALD) has been demonstrated to impart significant processing and performance gains in all areas of advanced materials in addition to semiconductor and other wafer applications. ALD is a well utilized platform technology for powders, porous particles, and high-surface area objects that has been widely demonstrated throughout the literature. Fundamentally, ALD on powders or any high surface area surface is the same as on flat surfaces. Simplistically, as long as the chemistry is self-limiting, the precursors can be kept separate and supplied at a concentration to saturate the available surface area, the thin film growth will be controlled and uniform. In practice, the very high surface area, long diffusion pathways, and complexities of gas solids mixing bring a few additional challenges not usually encountered during lab-scale ALD.

Historically ALD has been regarded as a lab-only process outside of semiconductor manufacturing, disregarded as too expensive and an unrealistic process for commercial adoption. However, several methods for high-throughput and scaled-batch manufacturing have been developed over the last decade, making ALD on powders affordable as a material-upgrading technique. Forge Nano has patented, constructed, and demonstrated the highest throughput ALD capability in the world, unlocking new potential for lower cost integration of ALD into products.

This tutorial will cover the basic equipment and process procedures for powder ALD at the lab scale, and equipment and particle ALD manufacturing methodologies. Additionally, it will provide some real-world examples of high surface area ALD applications in a spectrum of technologies ranging from pigments to catalysis and the most appropriate steps towards the industrialization of ALD-enabled materials for some of the application examples. The intent of this seminar is to identify the critical processing and scaling challenges for high surface area and powdered materials to enable more research opportunities and a greater breadth of commercial technology.

2:10pm **TS1-SuM-51 Closing Remarks & Thank You!***, **Scott Clendenning,*** Intel

Thank you for attending today's Tutorial Session! We will see you tomorrow at the Virtual Meeting!

Live Session
Room Live - Session LI-MoM
Plenary & Awards Live Session

Moderators: Prof. Sean Barry, Carleton University, Canada, Prof. Dr. Stacey Bent, Stanford University, Dr. Jane P. Chang, University of California, Los Angeles, Dr. Scott Clendenning, Intel Corporation, Dr. Thorsten Lill, Lam Research Corporation, Prof. Mikko Ritala, University of Helsinki

10:00am **LI-MoM-1 Opening Remarks & Welcome*, Scott Clendenning,*** Intel*; S. Barry,* Carleton University, Canada*; J. Chang,* University of California, Los Angeles*; T. Lill,* Lam Research Corp.

Welcome to the ALD/ALE 2021 Virtual Meeting! We hope you will enjoy the event1

10:10am **LI-MoM-3 Plenary Lecture: Materials & Innovation - Essential Elements that Underpin the Next Industrial Revolution*, Todd Younkin,*** SRC **INVITED**

All of us can see the next industrial revolution on the horizon. There are generational opportunities in hyperscaled computing, artificial intelligence (AI), autonomous driving, 5G/6G communications, integrated photonics, and even quantum computing and quantum sensing. Yet, as computing systems create new markets and move into these domains, the underlying hardware performance required to truly unleash these markets at scale is faced with constraints driven by fundamental physical limits. The opportunities of tomorrow are simply unachievable through anticipated hardware technologies and our old two dimensional (2D-) scaling playbook. A paradigm shift is underway to create new value propositions with semiconductor technologies and fabrication as the key drivers.

In response to this emerging crisis, SRC convened scientists from industry, academia, and government to outline a ten year R&D plan, the 2030 Decadal Plan for Semiconductors, as a scientific call to action.[1,2] Therein, we have outlined the global drivers and constraints for future information and communication technology (ICT) systems, providing goal-driven yet creative solutions to seek measured progress and real world impact. The document outlines five “seismic shifts” that are shaping the future of chip technologies for smart sensing, memory and storage, communication, security, and energy efficient computing.

At the heart of these advances lies chipmaking which requires materials innovation, new precursors, new chip fabrication equipment, an understanding of material interfaces, the continued development of process knowledge, and skilled workers that embody these essential elements. The tribal knowledge and research activity in these areas must evolve beyond 2D-scaling to contribute to heterogeneous and 3D-monolithic integration that is informed by a rapidly-changing state of the art in packaging and assembly, design, and novel ICT architectures.

In this talk, I will share my perspective on the evolving global R&D landscape for semiconductors, illustrate the five “seismic shift” drivers behind future ICT chip advances, and give specific examples of ALD- and ALE-based research that map to today’s and tomorrow’s efforts. I hope to leave the audience with a clearer picture of the needs and opportunities we see for the years ahead. The “Roaring 20s” will not be boring if you are interested in materials-driven semiconductor advances and are a disciplined imaginator!

[1] 2030 Decadal Plan for Semiconductors, https://www.src.org/about/decadal-plan/

[2] Newly-Announced $3.4 Billion Plan Aims to Stimulate US Semiconductor R&D, https://www.allaboutcircuits.com/news/newly-announced-3point4-billion-plan-aims-stimulate-us-semiconductor-rd/

10:40am **LI-MoM-9 Introduction to ALD and ALE Student Finalists*, Seán Barry,*** Carleton University, Canada*; J. Chang,* University of California, Los Angeles

We now introduce you to our 2021 ALD/ALE Student Award Finalists.

10:45am **LI-MoM-10 ALD Student Award Finalist Talk: Enhanced Surface Adsorption in Electric Field/Potential Assisted Atomic Layer Deposition (EA-ALD) of Ultrathin Ru Film*, Yoon Jeong Kim,*** *J. Han, J. Heo, T. Park,* Hanyang University, Korea

Ru metal has high work function of 4.7 eV, a low bulk resistivity (∼7 μΩ·cm). It has good thermal and chemical stability on metal state. Furthermore, Ru forms a conductive oxide phase, RuO_2, with work function of ~5 eV and resistivity as low as ~ 30 μΩ·cm, which prevents the formation of insulating interfacial layers in contact with oxides. As the size of semiconductor devices decreases, electronic applications require a nanometer-range of conformal thin film deposition in complex 3D structures. Among various thin film deposition technologies, atomic layer deposition (ALD) is considered to be promising in the development of nanometer device manufacturing technology due to its excellent step coverage and thickness control. [1]

However, continuous Ru film of under certain thickness (~6 nm) is difficult to form since they exhibit significant nucleation delay on various surfaces. The nucleation delay leads to increased process time and consumes a lot of precursor. For short nucleation delay time, high nucleation density is required.The high nucleation density forms continuous thin film with a smoother surface than obtained with low nucleation density. Therefore, the early nucleation density is important for metal film formation.

Using electric field/potential assisted atomic layer deposition (EA-ALD) can reduce the grain size and the critical thickness of the continuous film. When voltage is applied during precursor injection, it changes the surface potential of the substrate to promote chemical reactions. The electric field attracts the metal precursor molecules onto the substrate to improve the early nucleation density.As a result, the saturation of Ru layer density was increased on the substrate and a higher density thin film was deposited. It is possible to deposit continuous Ru ultrathin films with superior physical and electrical properties.

References [1] Chem. Mater. 2017, 29, 4654−4666

11:00am **LI-MoM-13 ALE Student Award Finalist Talk: Cryo-ALE of Silicon Based Materials*, Jack Nos,*** *G. Antoun, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; J. Faguet,* Tokyo Electron America Inc.,*; K. Maekawa,* TEL Technology Center America*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

Cryogenic Atomic Layer Etching (Cryo-ALE) has been presented in the previous ALE workshops (2019 & 2020) as a different approach to achieve ALE of SiO_2. In this process, C_4F_8 is injected in gas phase during the “modification” step, in order to physisorb on a cooled SiO_2 surface. The temperature window of this process was between -120°C and -90°C [1,2]. The etching is then achieved using an Ar plasma with a low energy ion bombardment. Nevertheless, the results were only reported on SiO_2 as no significant selectivity was observed over Si or Si_3N_4. Indeed, when using a fluorocarbon feed gas, the principle way to achieve a high selectivity of SiO_2 etch over Si or Si_3N_4 consists in creating a CF_X passivation layer on the surface of these materials. In cryo-ALE, as $C_4F_8$is injected in gas phase, $C_4F_8$is not dissociated and physisorption is not selective. Therefore, to try to etch other materials with higher selectivity, another gas chemistry has to be tested.

In 1996, Royer *et al.* studied the chemisorption of fluorine and sulfur on Si during a simultaneous exposure to SF_6 gas and Ne^+ ion beam. In this study, they showed by XPS measurements that the fluorine amount at the Si surface increases as the temperature decreases, for a process window between 20°C and –130°C [3]. In addition, it is well known that SF_6 plasma can be used to etch Si. For both reasons, SF_6 was chosen as a new feed gas instead of C_4F_8 to perform cryo-ALE of Si.

This work was carried out using a cryogenic ICP reactor. In-situ diagnostics are coupled to the reactor such as QMS and a Spectroscopic Ellipsometer. QMS measurements enabled to characterize the SF_6 physisorption and its surface residence time. SE measurements helped monitoring the thickness evolution over time during a process. Tests were performed on SiO_2, Si_3N_4 and p-Si coupons glued on SiO_2 6” carrier wafers.

First, SF_6 physisorption is studied and will be presented in order to optimize the process parameters, such as the temperature and the purge step time. Then, tests carried out on SiO_2 will be compared to the results obtained with C_4F_8. Finally, tests performed on Si will be reported showing the possibility to etch it over SiO_2.

These tests have hence enabled to prove that cryo-ALE can be achieved on different materials and that selectivity can be adjusted by changing the feed gas chemistry.

The authors would like to thank S. Tahara for all the helpful discussions.

This work was supported by CERTeM 2020 platform, which provides most of the equipment.

1. Antoun *et al.*, *Appl. Phys. Lett.***115**, 153109, 2019
2. Antoun *et al.*, *Sci. Rep.* 10, 2021
3. Royer *et al.,J. Vac. Sci. Technol. A***14**, 234–239, 1996

11:20am **LI-MoM-17 ALD Student Award Finalist Talk: What Controls the Conformality of Plasma ALD in High-Aspect-Ratio Applications?*, Karsten Arts,*** *S. Deijkers, T. Faraz,* Eindhoven University of Technology, Netherlands*; R. Puurunen,* Aalto University, Finland*; E. Kessels, H. Knoops,* Eindhoven University of Technology, Netherlands

This work discusses the role and impact of the plasma on film conformality during plasma ALD, using the material systems SiO_2 and TiO_2 as industry-relevant case studies. Specifically, detailed insight into the impact of radical recombination and ion bombardment is provided. This is essential for predicting and further advancing the film conformality, especially for future applications with extremely high-aspect-ratio (AR) features.

First of all, the loss of reactive plasma radicals through surface recombination is often considered a major factor limiting film conformality during plasma ALD. To pinpoint what level of film conformality can still be achieved, we have developed a method to determine the surface recombination probability r of the radicals.[1] This method is based on the film penetration into high-AR trench structures. For plasma ALD of SiO_2 and TiO_2 very low values of r~10^{-4} are determined, where r is observed to further decrease with temperature and pressure down to ~10^{-5}. Accordingly, film growth up to an AR as high as 200:1 or even 800:1 is achieved within reasonable cycle times, depending on temperature and pressure.[2] These results demonstrate that extremely challenging applications such as the coating of porous materials are feasible under specific process conditions.

Secondly, we demonstrate that ion bombardment can also have an important impact on film conformality during plasma ALD, even under mild plasma conditions with low-energy (<20 eV) ions. Specifically, it is observed that (low-energy) ions contribute to the film quality of SiO_2,[3] can induce crystallization during plasma ALD of TiO_2,[4] and can alter the growth per cycle by a factor of up to ~2 (for both SiO_2 and TiO_2). This can significantly affect the film conformality obtained on 3D nanostructures. Furthermore, we reveal that the magnitude of the influence of ions can be controlled by the ion energy dose, where a minimal effect is obtained when supplying a dose of <1 eV nm^{-2} $cycle^{-1}$, or a strong effect when supplying a dose of >100 eV nm^{-2} $cycle^{-1}$.[3,4]

In conclusion, we provide key insights that can further advance plasma ALD, particularly to meet the conformality requirements in demanding future applications.

1. K. Arts *et al*., J. Phys. Chem. C 123, 27030 (2019).
2. K. Arts *et al*., Oxygen recombination probability data for plasma-assisted atomic layer deposition of SiO_2 and TiO_2 (to be published)
3. K. Arts *et al*., Appl. Phys. Lett. 117, 031602 (2020).
4. K. Arts *et al*., Impact of ions on film conformality and crystallinity during plasma-assisted atomic layer deposition of TiO_2 (to be published).

11:35am **LI-MoM-20 ALE Student Award Finalist Talk: Modelling Atomic Layer Etching of Thin Film Metal Oxides*, Rita Mullins,*** Tyndall National Institute, University College Cork, Ireland*; S. Kondati Natarajan,* Synopsys , Denmark*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland

HfO_2 and ZrO_2 are two high-k materials that are crucial in semiconductor devices. Atomic level control of material processing is required for fabrication of thin films of these materials at nanoscale device sizes. Atomic layer deposition (ALD) and thermal atomic layer etching (ALE) allow fabrication of ultra-thin films for semiconductor device processing. ALD is a well-known metal oxide thin film deposition technique that enables a high level of control over film thickness. Thermal ALE, which is growing in importance, uses self-limiting halogenation (e.g. HF exposure) producing a non-volatile modified layer. Subsequent ligand exchange reactions remove up to a monolayer of the metal oxide. This modern approach for controlled etching is the reverse of ALD.

Given that it is difficult to investigate ALE reactions directly using experimental techniques, first-principles-based atomic-level simulations using density functional theory (DFT) can give deep insights into the precursor chemistry and the reactions that drive the etch of different materials. This contribution presents first-principles density functional theory modelling to examine the etch chemistry of thin films of HfO_2 and ZrO_2. HF exposures on the surfaces of HfO_2 and ZrO_2 are studied. HF coverages ranging from 1.0 ± 0.3 to 17.0 ± 0.3 HF/nm^2 are investigated and a mixture of molecularly and dissociatively adsorbed HF molecules is present at higher coverages. Theoretical etch rates of -0.61 ± 0.02 Å /cycle for HfO_2 and -0.57 ± 0.02 Å /cycle ZrO_2 were calculated using maximum coverages of 7.0 ± 0.3 and 6.5 ± 0.3 M-F bonds/nm^2 respectively (M = Hf, Zr). These calculations involve perfect, crystalline oxide substrates. To widen the scope of this work, we also compare the ALE chemistry using HF on amorphous HfO_2 and the chemistry using HCl as the first pulse reagent.

11:50am **LI-MoM-23 ALD Student Award Finalist Talk: Surface Passivation Using Aminosilanes for Area-Selective Atomic Layer Deposition*, Kaat Van Dongen,*** KU Leuven, Belgium*; R. Nye,* North Carolina State University*; D. De Simone, A. Delabie,* IMEC, Belgium

EUV lithography (EUVL) is one of the main drivers in the innovation of nano-electronic devices, as it can print structures of 14nm with a single exposure, and further downscaling is being studied. However, EUVL requires ultra-thin resist films to prevent pattern collapse, complicating the pattern transfer to the underlying layer. A possible solution is the combination of EUVL with area-selective deposition (ASD) of hard masks. ASD aims to deposit material only on the desired growth areas while no deposition occurs on the non-growth areas. ALD allows to deposit conformal films with atomic scale control, but most ALD processes have limited inherent selectivity. Surface passivation can improve the selectivity of ALD. Aminosilanes, such as dimethylamino trimethylsilane (DMATMS) and hexamethyldisilazane (HMDS), can work as passivating agents for SiO2 surfaces as trimethylsilyl (TMS) surface groups are introduced. To get a high selectivity, we need to optimize the TMS surface coverage and understand the impact on the passivation towards ALD.

We have therefore studied reactions of a hydroxylated SiO2 surface with DMATMS and HMDS and the effectiveness of the passivation towards TiO2 ALD (TiCl4/H2O). Both reactions are self-limiting, but the obtained TMS surface coverage is different. The reaction with DMATMS at 250°C saturates after 300 s and results in a TMS coverage of 2.1 TMS/nm2, close to theoretical limit of 2.41 TMS/nm2 (1), and a WCA of 101±1°. Lower temperature slightly reduces the WCA value (98±1° and 97±1° for 180°C and 135°C, respectively). This has only a minor effect on the selectivity for 3.41 nm TiO2 on the hydroxylated SiO2 (0.95, 0.92 and 0.90 for 250°C, 180°C and 135°C, respectively (RBS)). Contrarily, the HMDS reaction at 135°C and 180°C saturates after 600 s but the TMS coverage is at most 1.5 TMS/nm2 (XPS) and the WCA value is lower (80±6°). This leaves 0.9±0.7 OH/nm2 available for reaction with TiO2. The TiO2 selectivity is low, 0.13 for 3.41 nm TiO2 on the non-passivated SiO2. Possible explanations for the different surface coverage at saturation are the difference in chemistry, the HMDS could be too large to reach the remaining OH groups, or a difference in process conditions (e.g., partial pressure), since the reactions are carried out in different deposition tools. Sequential HMDS (180°C, 300s) and DMATMS (250°C, 300s) reactions result in a similar WCA but the selectivity towards TiO2 ALD drops faster compared to a single DMATMS reaction.

(1)Soethoudt, J. et al., J. Mater. Chem. C, 2019, 7, 11911

12:05pm **LI-MoM-26 ALD Student Award Finalist Talk: Electron-Enhanced Atomic Layer Deposition of Ruthenium Thin Films Using (DMBD)Ru(CO)$_3$*, Michael Collings,*** *S. George,* University of Colorado, Boulder

Electron-enhanced atomic layer deposition (EE-ALD) has been demonstrated as an effective method to rapidly nucleate and grow thin films at low temperatures [1,2]. During EE-ALD, electrons are used as a "reactant" in an ALD process. The role of the electrons is to remove surface ligands via electron stimulated desorption. In this work, EE-ALD was used to grow Ru thin films using dimethylbutadiene (DMBD) ruthenium tricarbonyl, or (DMBD)Ru(CO)$_3$, at low temperatures.

The sequential surface reactions for Ru EE-ALD are shown in Figure 1. During this reaction sequence, a hollow cathode plasma electron source (HC-PES) provided a high flux of electrons. The HC-PES is chemically robust and can operate at reactor pressures as large as 1 mTorr. Our HC-PES can emit electron currents ≥ 100 mA over surface areas of 50 cm^2. The electron energy employed for the Ru EE-ALD was 125 eV. Ru growth during EE-ALD was measured with in-situ spectroscopic ellipsometry. The Ru films were grown on silicon substrates with a native oxide.

Ru film growth was demonstrated at both 100°C and 160°C. Film thickness measured by ellipsometry showed that the Ru films nucleate and grow from the very first EE-ALD cycle. Linear film growth was observed over 600 cycles with growth rates of 0.17 Å/cycle and 0.23 Å/cycle at 100°C and 160°C, respectively. Spectroscopic ellipsometry measurements for 600 cycles of Ru EE-ALD at 160°C are shown in Figure 2. Self-limiting growth behavior was observed with respect to both $(DMBD)Ru(CO)_3$ and electron exposures. XPS was used to determine the purity of the Ru films. Oxygen was observed to be as low as 0.3 at%. Carbon was also low but could not be quantified because of the overlap of the C and Ru XPS peaks.

[1] Z.C. Sobell, A.S. Cavanagh and S.M. George, "Growth of Cobalt Films at Room Temperature Using Sequential Exposures of Cobalt Tricarbonyl Nitrosyl and Low Energy Electrons", *J. Vac. Sci. Technol. A***37**, 060906 (2019).

[2] J.K. Sprenger, H. Sun, A.S. Cavanagh, A. Roshko, P.T. Blanchard and S.M. George, "Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Boron Nitride Thin Films at Room Temperature and 100°C", *J. Phys. Chem. C***122**, 9455-9464 (2018).

12:20pm **LI-MoM-29 Plenary Lecture: Mechanisms of Thermal Atomic Layer Etching*, Steven George,*** University of Colorado Boulder **INVITED**

Atomic layer deposition (ALD) and atomic layer etching (ALE) are defined by two sequential, self-limiting surface reactions. ALE is based on surface modification by the first reactant. The second reactant then leads to volatile release of the modified surface. There are two types of ALE:plasma and thermal. Plasma ALE methods employ energetic ion or neutral species to release the modified material anisotropically using sputtering. Thermal ALE processes utilize gas species to release the modified material isotropically using thermal reactions [1]. Thermal ALE can be viewed as the "reverse of ALD".

One important mechanism for thermal ALE is surface modification by fluorination and volatile release by ligand-exchange reactions. Fluorination is thermochemically favorable because metal fluorides are more stable than metal oxides. The metal fluorides can then be volatilized when a ligand from an incoming metal precursor exchanges with F from the metal fluoride. This fluorination and ligand-exchange mechanism is applicable to the thermal ALE of many metal oxides such as Al_2O_3. Conversion reactions are able to extend the range of materials that can be etched using thermal ALE. Conversion reactions occur when an incoming metal precursor reacts with the surface of an initial material and converts the surface layer into another material. This new material may have etching pathways that were not accessible to the initial material.

Another thermal ALE mechanism is based on oxidation and ligand-addition reactions. This mechanism is particularly important for etching elemental metals. Oxidation first changes the oxidation state of the elemental metal. Subsequently, ligands can add to the oxidized metal center and form stable and volatile metal compounds. An example of oxidation and ligand-addition is thermal Ni ALE using SO_2Cl_2 and $P(CH_3)_3$. Chlorination by SO_2Cl_2 changes the oxidation state and then $P(CH_3)_3$ adds to the oxidized Ni center and forms volatile $NiCl_2(P(CH_3)_3)_2$.

Different mechanisms for thermal ALE can lead to selectivity in etching between various materials. Etching results if the sequential, self-limiting surface reactions produce stable and volatile compounds. Selectivity between materials occurs if the etching products for one material are not stable or volatile. A good example is the selectivity between Al_2O_3 and ZrO_2 using HF and $Al(CH_3)_3$ as the reactants. ZrO_2 is not etched and can be used to define a monolayer etch stop for the HF and $Al(CH_3)_3$ reactants.

[1] S.M. George, "Mechanisms of Thermal Atomic Layer Etching", *Acc. Chem. Res.* **53**, 1151 (2020).

12:55pm **LI-MoM-36 Introduction to 2021 ALD Innovator Awardee Stacey Bent, Stanford University, USA: Up, Down and All Around: Controlling Atomic Placement in ALD*, Seán Barry,*** Carleton University, Canada

With the increased importance of functional nanoscale materials for applications such as electronics, catalysts, and batteries, the interest in atomic layer deposition (ALD) as a method for fabricating structures with atomic-level control is intensifying. Based on sequential, self-limiting gas-surface reactions, ALD provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials while offering exceptional conformality, thickness control at the angstrom level, and tunable film composition. Yet despite the powerful film growth capabilities already attained with ALD, there is a compelling need to push the technique even further and control atomic placement not just in the direction of film growth, but also laterally. In this talk, I will describe research into the fundamental processes that drive ALD and ways to manipulate the chemistry to achieve area selective deposition, a bottom-up growth strategy in which deposition is directed only to desired regions of a patterned substrate. Mechanistically, the reaction chemistry of both the ALD precursor and the co-reactant at the growth surface play important roles in the ALD process and can influence both nucleation and growth. Importantly, by modifying the substrate properties, e.g., by the application of molecular monolayers or other surface treatments, the native reactivity of the surface with the ALD precursors can be altered to allow for area selective ALD. I will describe how area selectivity can be achieved across a range of different substrate and film materials, and also highlight challenges and potential solutions to reaching even high selectivities than currently possible.

1:00pm **LI-MoM-37 ALD Student Award Finalist Talk: Tuning Properties of Vapor Deposited ZIF-8 Thin Films With Preferred Orientation*, Marianne Kräuter,*** Graz University of Technology, Austria

Recent years saw a rise of solvent-free methods for synthesis of metal organic frameworks with the aim of accessing new application fields and facile processing. Since vapor deposition excels at these key points we employed a two-step chemical vapor deposition process, that allows for the delivery of high-quality, homogeneous thin films of zeolitic imidazole framework 8 (ZIF-8) from ZnO[1].

First, an ultrathin ZnO seed layer is deposited via plasma-enhanced atomic layer deposition (PE-ALD). Acting on the substrate temperature, ranging from room temperature to 200°C, the preferred crystal orientation can be switched from (100) to (002). ZIF-8 thin films are subsequently grown by subjecting the ZnO-layer to a 2-methyl imidazole vapor. To our knowledge, this is the first time that PE-ALD has been employed for the growth of ZIF-8.

To gain better control over the still novel deposition technique, the impact of crystal orientation and thickness of the ZnO precursor onto the resulting ZIF-8 thin films was investigated. The results show that ZIF-8 was successfully synthesized. Furthermore, X-ray diffraction studies reveal a powder-like structure together with a strong (100) orientation of ZIF-8 crystals. ZIF-8 coverage on the substrate increases for thicker ZnO layers with ZIF-8 particles exhibiting average thicknesses as high as (93 ± 9) nm for ZIF-8 from 3 nm ZnO and (192 ± 11) nm for ZIF-8 from 10 nm ZnO. The thickness increase during conversion rises to about 1600% as a function of ZnO thickness. ZnO orientation weakly influences the thickness increase during conversion and, via differing densities, also the crystallinity of the resulting ZIF-8. Our results provide vital knowledge about the link between deposition parameters of ZnO and properties of the resulting ZIF-8 thin films, namely coverage, thickness, roughness and orientation, thus making it possible to tailor them towards specific applications.

(1) Stassen, I.; Styles, M.; Grenci, G.; Van Gorp, H.; Vanderlinden, W.; De Feyter, S.; Falcaro, P.; De Vos, D.; Vereecken, P.; Ameloot, R. Chemical Vapour Deposition of Zeolitic Imidazolate Framework Thin Films. *Nat. Mater.***2016**, *15* (3), 304–310. https://doi.org/10.1038/nmat4509.

1:15pm **LI-MoM-40 ALE Student Award Finalist Talk: Reaction Pathways Leading to Anisotropic Pattering of Cu*, Xia (Gary) Sang,*** *M. Martirez, T. Smith, E. Carter, J. Chang,* University of California at Los Angeles

Plasma-thermal atomic layer etching (ALE) is a promising technique for enabling nanometer-level metal patterning. Utilizing the anisotropic nature of low energy ions, a modified layer is defined directionally in the plasma exposure step. The subsequently introduced isotropic etchant molecules only react with the modified region, leaving a final feature with ideal directionality and selectivity. This technique has been proven effective on patterning etch-resistant metals such as Ni.

In this work, the directional Cu etch is demonstrated with the plasma-thermal ALE process using low energy oxygen ions from an oxygen plasma to achieve directional modification and formic acid vapor to realize selective removal of the modified layer. This cyclic process yielded an etch rate of 2.4 nm/cycle at 80℃. The etch selectivity by gas-phase formic acid of copper oxide over metallic copper is high based on preliminary results and being quantified in this work. A 1.5 micrometer line structure with 55 nm Cu under a 135 nm thick SiCN hard mask was successfully patterned with high selectivity against the hard mask and relatively vertical sidewalls. The reaction products, postulated as copper formate (Cu(COOH)2), were measured by analyzing the condensates from the chemical vapor after the cyclic etching process with inductively coupled plasma mass spectroscopy (ICP-MS) and nuclear magnetic resonance (NMR). The surface chemical states after the etching process were quantified by XPS, showing the formation of Cu(I) and Cu(II) oxides upon oxygen plasma exposure and its subsequent removal after formic acid exposure, with the percentage of Cu(OH)2 increased after the vapor was introduced to the surface. To corroborate these findings, density Functional Theory (DFT) calculations were carried with experimental conditions. It was found that a water-free dimeric tetra(μ-formato)dicopper(II) "paddlewheel" complex (Cu2(HCOO)4) is the most favorable etching product, with its formation reaching equilibrium conditions from Cu(II). The most likely precursor for the dimer is the diformatodi(formic acid)copper(II) monomer, which favorably dimerizes under the same water-lean condition at which the dimer persists. Finally, DFT simulation is compared to the NMR measurements.

1:30pm **LI-MoM-43 ALE Student Award Finalist Talk: Thermal Atomic Layer Etching of Cobalt Using SO_2Cl_2 and $P(CH_3)_3$***, Jessica Murdzek*, *S. George,* University of Colorado Boulder

Thermal metal ALE is challenging because the oxidation state of the volatile metal etch products are usually different than the zero oxidation state of the elemental metal.In this work, cobalt ALE was developed by first oxidizing the cobalt via chlorination using SO_2Cl_2. Then the Co was etched by the binding of trimethyl phosphine (PMe_3) ligands that can volatilize the cobalt chloride.Thermal Co ALE was achieved at 150 °C by properly balancing the SO_2Cl_2 exposures that chlorinate cobalt and the PMe_3 exposures that remove the cobalt chloride (Figure 1).

The logic of this approach is based on the Covalent Bond Classification (CBC) method.The CBC method indicates that most organo-metallic complexes obey the 18 or 16 electron rule. We have shown previously that this method works for the thermal ALE of nickel. In the CBC method, a chloride ligand donates one electron to the metal center and is referred to as an X ligand. PMe_3 is a two-electron donor and is designated an L ligand. The nickel ALE process was accomplished using these sequential steps: chlorination to $NiCl_2$ and ligand addition to form NiX_2L_2, or $NiCl_2P(Me_3)_2$, resulting in an etch process. For cobalt, the most likely compounds to be created using chloride and trimethyl phosphine ligands are CoX_2L_4, CoX_2L_2, or CoX_3L_3. These compounds have cobalt in the +2 or +3 oxidation states.

Co ALE process was demonstrated with SO_2Cl_2 and PMe_3 exposures at 150 °C using in situ quartz crystal microbalance (QCM) measurements. The QCM experiments indicated that cobalt very readily chlorinates when exposed to SO_2Cl_2. A typical mass gain with one exposure of SO_2Cl_2 on cobalt can be up to 1400 ng/cm^2.In contrast, an identical exposure of SO_2Cl_2 on nickel results in a mass gain of only 100-150 ng/cm^2. The PMe_3 step was also different on cobalt when compared with nickel. For nickel ALE, one exposure of PMe_3 removes all available $NiCl_2$. An identical exposure of PMe_3 on $CoCl_2$ only removes ~20% of the available $CoCl_2$.Consequently, multiple PMe_3 exposures are required to remove the $CoCl_2$.

Co ALE requires a careful balance between the SO_2Cl_2 and PMe_3 exposures.Too much cobalt chlorination with SO_2Cl_2 will lead to difficulties removing all the cobalt chloride with PMe_3.Cobalt chloride that is not removed during one ALE cycle will build up and a cobalt chloride top layer will grow with successive ALE cycles.Optimizing Co ALE was based on determining the number of PMe_3 exposures required to remove the top cobalt chloride layer.Using the optimum exposures of SO_2Cl_2 and PMe_3 results in high etch rates for cobalt ALE of 3-5 Å/cycle at 150 °C (Figure 2).

1:45pm **LI-MoM-46 ALD Student Award Finalist Talk: Insight into Film Growth Mechanisms in Polyurea Molecular Layer Deposition (MLD) Using New and Combined Precursors***, **Siyao Wang***, *R. Nye, G. Parsons,* North Carolina State University

Analogous to atomic layer deposition (ALD), organic molecular layer deposition (MLD), enabling controlled deposition of materials at the molecular level, has emerged in recent years as a vapor phase method for depositing ultrathin polymeric films to be used in microelectronics, catalysts, and battery electrodes etc. However, lack of fundamental understanding in film growth behavior and underlying mechanisms is still impeding further development and application of MLD. In this study, our goal is to gain understanding on deposition mechanisms to achieve better control over film properties by employing new and innovative combinations of MLD precursors, with the aid of in situ characterization capability and the establishment of a kinetic model.

Specifically, we choose four polyurea precursors including p-phenylene diisocyanate (PDIC), 1,6-hexamethylenediisocyanate (HDIC), ethylenediamine (ED) and 1,6-hexanediamine (HD), in which HDIC is utilized for the first time to deposit MLD films, and proves to be a feasible alternative with improved thermal stability compared to PDIC. The polyurea films are deposited on hydroxylated SiO2 substrates at 45 °C-60 °C and measured every cycle using in situ ellipsometry (every ten cycles for PDIC/HD). As shown in Figure 1, accelerated initial growth within the first ~20 cycles is observed for all films, followed by a steady growth regime. Significantly higher growth at the initial stage is attributed to the higher density of reactive sites on the starting SiO2 surface. As growth proceeds and polymer chains become more entwined, the active site density decreases due to site-terminating double reactions (DRs) and site blocking, which leads to a decrease in growth rate. The steady growth rates for each polymer increase with precursor rigidity, with 0.32, 0.13, 0.020, and 0.020 nm/cycle for PDIC/ED, PDIC/HD, HDIC/ED, and HDIC/HD, respectively, consistent with more prevalent DRs for more flexible polymers.

To further explore the growth initiation and transition mechanism, we deposit hybrid polyurea films by alternating precursors. As shown in Figure 2, when deposited on HDIC/ED substrate, PDIC/ED films exhibit an accelerated thickness increase followed by a subsequent decrease to steady growth rate, due to competition between reactive site regeneration and consumption. Additionally, to describe and predict growth behavior, a model with a simple decay parameter is established (Figure 1). Meanwhile, more advanced modeling based on reactive site termination and generation rates is being constructed to gain fundamental knowledge on growth mechanisms, facilitating future depositions of unique precursors and combinations.

2:00pm **LI-MoM-49 Closing Remarks & Thank Yous***, J. Chang,* University of California, Los Angeles*; **Thorsten Lill,*** Lam Research Corp.*; S. Barry,* Carleton University, Canada*; S. Clendenning,* Intel

Thank you for attending today's Plenary and Award Session. We will see you tomorrow!

Live Session
Room Live - Session LI-ALD-TuM1
Precursors (AF): ALD Processes Live Session

Moderators: Prof. Jin-Seong Park, Hanyang University, Dr. Tania Sandoval, Technical University Federico Santa Maria, Dr. Matthias Young, University of Missouri-Columbia

9:30am **LI-ALD-TuM1-1 Welcome, Thank Yous & Session Instructions***, **Jin-Seong Park**, Hanyang University, Korea (Republic of)*

Thank you for attending and we hope you will enjoy the session!

9:35am **LI-ALD-TuM1-2 Atomic Layer Deposition of Amorphous/Nanocrystalline Phase-Composite Nanolayers***, **Myung-Mo Sung**,* Hanyang University, Republic of Korea **INVITED**

Interparticle electronic coupling is essential for quantum dot solids to fulfill its expected wide-tunable electrical and optoelectrical properties but has been limited by disorder. Here, we approach alternatively to disorder-immune coupling by synthesizing quantum dot solids based on amorphous/nanocrystalline phase-composite monolayers. The ZnO amorphous matrix, which infills voids of the less regularly ordered ZnO nanocrystal array, mediates electronic coupling between neighboring quantum-confined nanocrystals by means of resonant wavefunction overlap generating a quantized conducting state without forming tunneling barriers. Thin-film transistors based on the phase-composite semiconductors show delocalized band-like transport with superior field-effect mobility value compared to amorphous or polycrystalline ZnO semiconductors. Calculation of charge transport properties is executed using non-equilibrium Green's function method under various degrees of disorder. For two distinct types of phase-composite quantum dot solids, embedding periodic and disordered nanocrystals, the reproduced conductivities are unexpectedly comparable because the amorphous-mediated interparticle coupling is tolerant against disorder-induced degradation. Furthermore, this facile and stable coupling demonstrates wafer-scale uniform deposition and bias-illumination stability of our phase-composite quantum dot solids.

9:55am **LI-ALD-TuM1-6 Density Functional Study on ALD Precursors for Hexagonal Boron Nitride Deposition***, **Naoya Uene**, T. Mabuchi,* Tohoku University, Japan*; J. Yong,* Japan Advanced Chemicals Ltd., China*; M. Zaitsu, S. Yasuhara,* Japan Advanced Chemicals Ltd., Japan*; T. Tokumasu,* Tohoku University, Japan

Hexagonal BN (*h*-BN) has been considered as a promising dielectric film for 2D material-based electronics because of its atomically smooth and charge-free interface with an in-plane lattice constant similar to that of graphene. The atomic layer deposition (ALD) technique is a way to deposit conformal and ultrathin dielectrics directly on insulators or semiconductors at relatively low temperatures than a catalytic CVD process.

The purpose of this study is to provide a path to a new precursor design through theoretical investigations on several precursor's stabilities used in BN-ALD. At present, there are only a few types of BN-ALD precursors that satisfy favorable characteristics and no studies that systematically verify their stability as far as we know. The systematic and theoretical investigation of the BN-ALD precursor is also helpful for engineeringly critical nitride deposition processes such as TiN, AlN, and GaN.Herein, the BN-ALD using BCl_3 and $B(NMe_2)_3$ precursors on OH terminated SiO_2 substrates was studied. They have been attractive precursors for depositing ultra-thin dielectrics and are relatively easy to simulate.

All DFT calculations were performed within spin-polarized generalized gradient approximation (GGA) parameterized by Perdew–Burke–Ernzerhof (PBE) exchange–correlation as implemented in Materials Studio 2018 software Dmol^3 packages. The average bond length of B–Cl is found to be 1.734 Å, which is in good agreement with 1.794 Å in the previous study at the MP2 level. Also, in $B(NMe_2)_3$, the average bond length of B–N is 1.433 Å, and C–N is 1.431 Å. These calculations also show that the both structures are very symmetrical. From a bond energy calculation, 114.7–114.8 kcal/mol is obtained for the B–Cl bond in BCl_3. In $B(NMe_2)_3$, 105.6–105.7 kcal/mol for B–N bond and 88.3–88.4 kcal/mol C–N bond are obtained. These results indicate that both precursors are sufficiently stable at room temperature. The $B(NMe_2)_3$ thermally decomposes at lower temperatures than BCl_3, and organic precursors may be more suitable for low-temperature processes. Further studies are planned on the effect of ligand type on bond energy in BN precursors. Besides, we will investigate the kinetic stability by obtaining an activation barrier for providing the way to a new precursor design.

10:10am **LI-ALD-TuM1-9 A Novel co-Precursor Approach for Atomic Layer Deposition of Various Semiconductor Thin Films***, **Kok Chew Tan**,* Soulbrain, Korea (Republic of)*; J. Jung, C. Yeon,* Soulbrain , Korea (Republic of)*; J. Kim, J. Kim,* Soulbrain, Korea (Republic of)*; S. Kim, T. Eom,* Soulbrain , Korea (Republic of)*; S. Lee,* Soulbrain , Korea (Republic of)*; Y. Park,* Soulbrain , Korea (Republic of)

Film quality and conformality are some of the critical concerns in deposition technology, especially in ever increasing complex geometry such as high aspect ratio feature and three dimensional (3D) device. In this work, we present an innovative approach that involves an additional step of co-precursor pulse in conventional atomic layer deposition (ALD) process to overcome challenges of depositing high quality and conformal thin films. One of the key ideas of this co-precursor pulse is to induce ligand exchange with the main precursor, which leads to desirable effects on the film quality in terms of impurity contents, density, surface roughness and crystallinity. In addition, film growth rate could be controlled by altering the pulsing sequence of co-precursor in ALD process cycle. This strategy enables considerable improvement in film conformality, particularly in high aspect ratio feature.

Our experimental evidences demonstrate wide applicability of this innovative approach in various areas, for example: in ALD of nitride film, high-*k* oxide film and MoN_x film. By pulsing co-precursor in ALD process, **Fig. 1** shows a noticeable 50% improvement in TiN film resistivity due partly to large decrease in Cl impurity of more than 50% as determined by SIMS depth profiles **[1]**. For ALD of high-*k* oxide (HfO_2) film at 320°C, in addition to the improvements in film density and significant 58% decrease in carbon impurity, co-precursor pulse in ALD is also capable of enhancing high-*k* dielectric film electrical performances, with 20% reduction in leakage currents and 8% increase in capacitance, as demonstrated in **Fig. 2a**. In terms of the effects of co-precursor pulse on ALD of MoN_x, **Fig. 3** reveals improvement in film resistivity at deposition temperatures of 380, 400 and 420°C, with the largest observable improvement of 46% at 420°C. All experimental results exhibit improved step coverage which are made possible by this innovative approach, for example as illustrated in **Fig. 2b**.

All these findings give clear evidences of the promising capability of co-precursor pulse in ALD for achieving superior film quality, high film conformality and excellent electrical performances. This innovative approach of co-precursor pulse in ALD process could open up various opportunities in applications such as low resistive metal gate interconnects for future technology node, high aspect ratio 3D metal-insulator-metal (MIM) capacitor, DRAM trench capacitor, and other 3D device architectures such as 3D gate-all-around (GAA) and 3D NAND.

Reference:

5. C. Yeon, J. Jung, H. Byun, K.C. Tan, T. Song, S. Kim, J.H. Kim, S.J. Lee and Y. Park, AIP Advances 11, 015218 (2021).

10:25am **LI-ALD-TuM1-12 Tuneable YAlOx Protective Coatings Against Plasma Damage to Meet the Requirements in Future Semiconductor Fabrication Processes***, J. Kalliomaki, M. Kaaria, K. Dorai, **Tiina McKee**,* Picosun Oy, Finland

Atomic Layer Deposition (ALD) enabled corrosion protection solutions against plasma etch are becoming more sought after in the semiconductor industry. Current wafer fabrication process flows include several steps where plasma etching is necessary. An inevitable consequence of using such strong etching chemicals is that the tool itself will be etched. This tool damage can be managed by applying a corrosion-resistant coating to the etch tool to minimize plasma damage [1]. ALD is especially useful for coating tool components having 3D or high aspect ratio features. Nevertheless, even there are challenges. A common industrial solution is several-hundred-nm-thick Y_2O_3 film, which by ALD tends to be a very hygroscopic film product as-deposited. If the ALD deposition uses H_2O as a co-reactant, the deposited material will retain some of that H_2O and releases it during the subsequent Y-precursor pulse causing CVD-like growth [2]. This phenomenon becomes more pronounced as the film thickness increases, making it difficult to accurately control the process. Another option would be to completely purge the H_2O and stay within the ALD regime, but that makes the processing times unfeasibly long for an industrial solution.

Our approach is to combine the highly-etch-resistant Y_2O_3 ALD process with more robust ALD processes, such as Al_2O_3 or ZrO_2. It has been shown that to gain most of the benefits from Y_2O_3 its molar concentration can be less than half in a composite oxide [3]. Here we demonstrate that a high performance ALD corrosion barrier deposition with the speed and convenience of Al_2O_3 process and durability of Y_2O_3 can be achieved by carefully controlling the film composition, and that the process is transferrable to an industrial scale deposition chamber.

This study shows how fluorine-based plasma etch rate results from films deposited in a batch ALD tool (Picosun P-300B) at 300 °C correlates with the composition of the oxide film and suggests reasonable compromises between extremely low plasma etch rates and throughput and conformality of the ALD process. The variance in composition was made by altering the ratio between Al_2O_3 and Y_2O_3 cycles in the recipe. The etching was made with CF_4/O_2 plasma to determine the etch rate. The results suggest that by making a compromise to increase the etch rate by factor of 1.5, we can gain an order of magnitude benefit in throughput, film uniformity and conformality. This can be translated to a significant reduction of manufacturing costs by increasing the maintenance interval of etch tools.

1 Shih, ISBN: 978-953-51-0467-4

2 Abdulagatov et al., doi:10.1134/S1063739719010025

3 Kim et al., doi:10.1111/j.1551-2916.2011.04589.x

10:50am **LI-ALD-TuM1-17 ALD of Boron Nitride by Polymer Derived Ceramics chemistry***, W. Hao, T. Saboo, C. Journet,* ***Catherine Marichy****,* Univ Lyon, France **INVITED**

Scientific interest for hexagonal boron nitride (h-BN) material, especially as thin film and nano-/hetero-structures, is growing due to its potential use in various domains such as microelectronic, energy and environment. Atomic Layer Deposition (ALD) is a technique of choice for fabrication of such thin films and complex nanostructured material. Some ALD processes of BN have been reported; mostly based on ammonia and/or halide precursors. In all cases, the crystalline quality of the as-deposited layers remains insufficient and post-annealing treatments are currently performed. Despite these limitations, ALD already demonstrates suited to fabricate BN layers that can successfully be integrated into electronic devices. Based on polymer derived ceramics chemistry, we developed a two-step ALD process of BN that permits access to various BN thin films and complex nano-/hetero-structures. It consists of the growth layer by layer of a preceramic BN films, onto various substrates, at low temperature, and then to its densification into pure BN by annealing process.

Herein, the potential of the ALD process based on PDCs route for BN thin films will be discussed. Indeed, BN thin films were successfully deposited in a controlled manner on various inorganic and organic substrates/templates. In particular, functional quality crystalline BN nano/heterostructures have been fabricated using substrates or templates with different dimensionalities. Their applications as protective coatings as well as filters and absorbers to purify polluted water from organic/oil have been investigated. The involved mechanism will be also introduced.

11:10am **LI-ALD-TuM1-21 Process Parameter and Substrate Dependence of Sticking Coefficients in Atomic Layer Deposition Processes***,* ***Martin Knaut,*** TU Dresden, Germany*; L. Jäckel,* Fraunhofer ENAS, Germany*; M. Albert, T. Mikolajick,* TU Dresden, Germany

Surface reaction probabilities in atomic layer deposition (ALD) processes are often described by simplified sticking coefficients. For ALD processes carried out with sufficiently high reactant doses to enable saturated and self-limiting surface reactions these sticking coefficients are only of minor interest. As a measure of how many surface interactions are necessary for a successful chemisorption they mainly quantify the efficiency of a process. Consequently, knowledge about sticking coefficients can help to make processes more efficient or to select the most cost-effective chemistry. These aspects are becoming increasingly important for the coating of porous materials and three-dimensional structures. Such demanding substrates are much more sensitive to surface reaction probabilities and insufficient reactant doses may result in thickness profiles which strongly depend on the sticking coefficients. This sensitivity was used to investigate the sticking coefficients of alumina and tantalum nitride ALD processes by analyzing thickness profiles grown in a narrow gap between two silicon wafers. The narrow gap impedes the transport of reactants which can generate an unsaturated coating with a transition from a fully coated wafer edge to an uncoated wafer center. Based on the thickness profiles measured by scanning spectroscopic ellipsometry predictions about the sticking coefficients can be made with regard to process parameters, precursor chemistry and substrate properties.

In this paper the experimental results regarding the sticking coefficients during the initial and the homogeneous film growth of alumina or tantalum nitride on wafers with different reactive surface groups are presented and discussed. The experiments confirmed the dependence of the sticking coefficients from process parameters like co-reactants, doses and temperatures as well as different film growth mechanisms for the heterogeneous growth on a substrate material and the homogeneous layer-by-layer growth. The differing sticking coefficients were investigated by analyzing the characteristic thickness profiles during the initial film growth and after the transition to the homogeneous film growth. Pre-coated test wafer were used to verify these effects and to separate process parameter and substrate impacts.

The applied approach is presented as a simple and versatile tool to study novel precursors and processes and to investigate substrate effects on the ALD film growth. Further, the attainable findings can help to improve processes and to adapt them to specific substrates and demanding surface topographies.

11:25am **LI-ALD-TuM1-24 Volatile Cerium and Ytterbium Precursors for Atomic Layer Deposition: Synthesis, DFT and Application***,* ***Parmish Kaur,*** Ruhr University Bochum, Germany*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; R. Ghiyasi,* Aalto University, Finland*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Cerium-containing thin films find a broad range of applications in diverse areas such as catalysis, sensors, solid oxide fuel cells, water splitting, possible high-*k* gate dielectric material to name a few. Ytterbium-containing films have attracted increasing attention for the advancement of semiconductor devices such as Ytterbium-doped optical fibers that are useful for high power laser applications. Atomic layer deposition (ALD) is an appealing technique to grow high-quality thin films with precise thickness control and large area homogeneity. However, there are a limited number of suitable ALD precursors for Ce and Yb and thus new metalorganic precursors are much sought after.

Herein, we report a systematic study on the rational development of homoleptic tris-guanidinate $[Ln(guan)_3]$ and tris-amidinate $[Ln(amd)_3]$ where the lanthanide Ln = Ce and Yb.[2] The C on the N-C-N backbone is functionalised with Me, NMe_2, NEt_2; (Me=methyl, Et=ethyl) and N is functionalised with symmetrical iso-propyl (^iPr) and asymmetrical tertiary-butyl (^tBu) and Et groups (Figure 1) to study their influence on the physicochemical properties. The compounds are analyzed for their structure, spectroscopic purity, and composition. The solid-state structures obtained for guanidinates of Ce and Yb reveal the monomeric nature of the compounds and the reactive M-N bonds present could be favourable for ALD. Thermogravimetric (TG) studies show that the complexes are volatile, and the symmetrical complexes are thermally more stable than asymmetrical ones. Density functional theory (DFT) modelling is performed to study the reactivity of the complexes with water and molecular oxygen. It is found that in the presence of water, tris-guanidinates are more reactive than tris-amidinates and the Ce complexes are even reactive with molecular oxygen. As a representative precursor for ALD, $[Ce(dpdmg)_3]$ is used for the deposition of CeO_2 using water as the co-reactant. The process yielded polycrystalline CeO_2 films on Si(100) substrates at 160 °C deposition temperature and thin-film analysis is done using XRR, GIXRD, XPS, UV-Vis spectroscopy. While the GIXRD analysis revealed no other peaks except those for the CeO_2 phase, the XPS analysis indicated beside the Ce^{4+} features, an evidence of co-existence of some Ce^{3+} features in the films. (Figure 2). This study further confirms that the nitrogen coordinated lanthanide complexes are very appealing for ALD applications.

1. https://www.atomiclimits.com/alddatabase/

2. P. Kaur, L. Mai, A. Muriqi, D. Zanders, R. Ghiyasi, M. Safdar, N. Boysen, M. Winter, M. Nolan, M. Karppinen, A. Devi, *Chem. Eur. J.***2021**, *27*, 1–15. DOI: 10.1002/chem.202005268

11:40am **LI-ALD-TuM1-27 Predicting Precursor Volatility With Machine Learning***,* ***Simon D. Elliott****, A. Chandrasinghe, A. Chandrasekaran, Y. An, M. Halls,* Schrödinger

The success of deposition and etch processes depends crucially on the properties of the metalorganic precursor chemicals and much innovation in this field centers around developing new precursors. The space of possible ligands is vast, much too large to be explored systematically in the lab. The area is therefore ripe for computational screening and design, as long as the relevant properties can be computed quickly and accurately.

Volatility is a key property for vapor-based deposition or etch processes, but one that is difficult to compute from first principles. Here we utilize a machine learning (ML) approach to train surrogate models for pressure-temperature relationships. The first step involves the curation of volatility data from experimental vapor pressure curves for over 1,000 purely organic molecules. A variety of ML algorithms (Random Forest, Neural Networks *etc.*) are studied in conjunction with different chemoinformatic descriptors and fingerprints. The trained ML model is capable of predicting the evaporation temperatures for 1 Torr and 10 Torr partial pressure of the organic compounds with a mean error of 25°C. We show how the model may be applied to metalorganic complexes, accounting mostly for the intermolecular interaction between ligand shells. The ML model not only allows the identification of salient molecular descriptors but also provides insights to extend the approach to more accurately include the effect of the metal center. We discuss the prospects for informatics-based design and optimization of specialty chemicals.

11:55am **LI-ALD-TuM1-30 Surface Chemistry of Deposition and Etch from First Principles Simulations*, Michael Nolan,*** Tyndall Institute, Ireland **INVITED**

First principles simulations are a powerful tool to enable the investigation of surface chemistries and since atomic level processing is driven by self-limiting surface chemistries simulations can provide deep insights into Atomic Layer Deposition, Molecular Layer Deposition and Atomic Layer Etch. Key information is obtained from modelling the elementary steps of a process, including precursor adsorption, ligand elimination and substrate chemistry. In this contribution, we will discuss our work on first principles modelling of ALD, MLD and ALE processes.

For ALD, we present DFT studies of Co and Ru PEALD (using H2/Nitrogen), for future interconnects in which Co and Ru replace Cu or be incorporated into TaN to give thinner barrier/liner stacks [1-4]. The post-plasma metal surface is modelled as an NH/NH2-terminated surface [1] with predicted composition under ALD conditions. We explore Ru(Cp)2 and Co(Cp)2 precursors and their chemistry on nitrided surfaces- ligand elimination, the role of multiple precursors and coverage. Initial results on the chemistry of plasma species is presented to explore how ligands are eliminated.

For MLD, we present an overview of our DFT work on the chemistry of metalcone growth [5,6], highlighting insights into the impact of the organic precursor on MLD growth; in particular differences between bifunctional ethylene glycol and glycerol . The chemistry at different oxides will also be discussed.

We discuss our studies of ALE of W [7] and Co [8]. For W we present a detailed analysis of the chemistry in a process using partial metal oxidation and WClx half-reactions. For Cp, we discuss the development of a process chemistry that uses mild oxidation agents and CO to promote etching.

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12:30pm **LI-ALD-TuM1-37 Atomic Layer Deposition of Functional Dielectrics and Metals for the Emerging Non-Volatile Memories*, Anna Chernikova,*** *M. Kozodaev, R. Khakimov, Y. Lebedinskii, A. Markeev,* Moscow Institute of Physics and Technology, Russian Federation **INVITED**

Since the first discovery of ferroelectricity in nanometer-scale hafnium oxide (HfO_2) it is considered very attractive for the emerging non-volatile ferroelectric random access memory (FeRAM). A notable feature of ferroelectric HfO_2 is complete compatibility with the semiconductor fabrication process. Besides the technologically suitable intrinsic properties of HfO_2, atomic layer deposition (ALD) may be successfully applied for its growth. Moreover, TiN, which usually serves as top and bottom electrodes for HfO_2-based FeRAM stacks, is also routinely grown by ALD. However, TiN is chemically reactive and readily oxidizes during ferroelectric film crystallization leading to the formation of the oxygen-poor interface with HfO_2-based films. Eventually, it causes instability of ferroelectric response, revealing itself in some undesired features of ferroelectric capacitors as wake-up, imprint, etc. The natural demand for electrode materials replacement faces some challenges. The ferroelectric response of HfO2-based stacks depends on many factors, including the electrodes' crystallinity, morphology, chemical properties of the interfaces, etc. Moreover, the cross-correlation between the effect of the electrodes and intrinsic properties of the given HfO_2-based film, determined by the dopant element and concentration, thickness, etc, is expected.

Thus, the search for better electrodes and HfO2-based ferroelectric film combination is still outgoing. Considering the ferroelectric material ALD provides the great possibility to improve the ferroelectric response due to the high level of doping control. Regarding the electrodes noble metals and their oxides, which can be also grown by ALD, are especially promising because they can resist oxidation during FeRAM stack manufacture.

In this work, the possibility to utilize Ru/RuO_2 electrodes and complex doped HfO_2-ZrO_2 oxides, both grown by ALD to improve the ferroelectric properties of capacitors is discussed. Special attention is paid to the ability to control the interface properties between electrodes and ferroelectric films by the ALD conditions and to the effect of the electrodes on the crystalline structure of the different HfO_2-based films grown by ALD.

12:50pm **LI-ALD-TuM1-41 Crystallinity Control via Atomic Level Scaffolding*, Elham Rafie Borujeny,*** *K. Cadien,* University of Alberta, Canada

Conventional methods for the growth of epitaxial thin films rely on the crystallographic relationship between the growing film and the underlying substrate. For the case of homoepitaxy (i.e., where the film and the substrate consist of the same material), achieving high quality crystalline films is relatively easy and can be facilitated by providing adequate energy for the deposition process using, for example, higher deposition temperatures, plasma-assisted processes, and laser-assisted processes. On the other hand, for the case of heteroepitaxy (i.e., where the film and the substrate consist of different materials), achieving the desired crystallinity of the thin film is much more challenging specially in cases where a suitable substrate that can induce a certain crystal structure in the growing film is either not accessible or not technologically useful.

In this work, we provide a strategy to precisely control the crystallinity of the ALD films by creating atomic scale scaffolds that can steer the atoms into forming the desired film crystal structure during the deposition process and minimize the role of the substrate in achieving film crystallinity. We explain the criteria for choosing the scaffold and elaborate on the unique role of ALD in exploiting the potentials of the atomic level scaffolding strategy in growing crystalline phases of technologically important thin films. We show that creating the atomic scale scaffold can be easily incorporated into the conventional ALD cycles by adding additional dose and purge steps therefore making it possible to seamlessly integrate this scaffolding process into conventional ALD processes.

This work is especially important in heteroepitaxy where minimizing the role of the substrate as a result of this scaffolding strategy provides a means by which metastable and stable phases of materials in thin film form could be grown on foreign substrates that were not conventionally possible.

1:05pm **LI-ALD-TuM1-44 Plasma-Enhanced Atomic Layer Deposition of Copper Oxide Semiconductors With Tunable Phase, Oxidation State, and Morphology for P-Type Thin Film Transistors*, Julia D. Lenef,*** *J. Jo, O. Trejo,* University of Michigan, Ann Arbor*; D. Mandia ,* Argonne National Laboratory, USA*; R. Peterson, N. Dasgupta ,* University of Michigan, Ann Arbor

Although advances in p-type metal oxide semiconductors are more infrequently reported than their n-type counterparts, Cu_2O—a p-type metal oxide—has been shown to be a viable candidate due to its moderate optical bandgap (2.0-2.6 eV)[1] and high measured Hall mobility (> 100 cm^2/V-s).[2] Previous works indicate that grain size, crystallinity, oxidation state, and phaseof the CuO_x films directly impact the resulting electronic properties for devices such as solar cells and thin film transistors. However, little work has been done to (1) obtain precise control over phase, oxidation and morphology and (2) explore the coupled effects between the materials synthesis, film structure and composition on the p-type semiconducting properties.

To address this knowledge gap, plasma-enhanced atomic layer deposition (PE-ALD) of CuO_x was performed with select ratios of hydrogen and oxygen plasma and a non-fluorinated copper amidinate precursor.[3] The phase of CuO_x was successfully controlled to synthesize Cu, Cu_2O, or CuO, verified by grazing-incidence x-ray diffraction. Furthermore, post-deposition annealing of the as-deposited films provides an additional process knob to tune the phase, oxidation state and morphology. Vacuum annealing resulted in up to a ~8 times increase in the grain size, and reduction in the copper oxidation state quantified by atomic force microscopy and synchrotron x-ray absorption spectroscopy, respectively. Next, to correlate the process-structure relationships observed with the p-type semiconductor properties, bottom-gate TFTs were constructed, and a maximum mobility (~0.01 cm^2/V-s) and on/off current ratio of (~10^5) for PE-ALD films was achieved for films with the largest Cu(I) content and grain size.

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1:20pm **LI-ALD-TuM1-47 Tuning Coercive Field and Polarization in Inherently Ferroelectric HZO Film Deposited Using HfD-04 and ZrD-04***, **Raisul Islam**, M. McBriarty, M. Laudato, R. Clarke, S. Hoang, C. Chen, G. Panaman, K. Littau,* EMD Electronics, USA

Data transfer throughput in off-chip memory devices are bottlenecked by the “memory wall”, where the data movement throughput does not scale with the technology node, and which cannot be solved by the current on-chip solutions like SRAM because of its large area requirement. Ferroelectric memory devices utilizing the switching of the polarization of electric dipoles in certain materials can offer ultra-low energy switching, scalability and they are on-chip BEOL compatible making them attractive for neuromorphic computing application. Alloys of HfO_2 and ZrO_2, $Hf_{0.5}Zr_{0.5}O_2$ (HZO), are shown to have excellent ferroelectricity and are CMOS compatible, making them one of the most widely studied FE materials for memory applications.

In this paper, inherently ferroelectric HZO was demonstrated, deposited by atomic layer deposition using the alternating pulsing of HfD-04 and ZrD-04 precursors with ozone as the reactant. We observed that the ALD window (300 °C-400 °C) is wide and higher in deposition temperature compared to some other Hf and Zr precursors. This wide temperature window allows the FE orthorhombic phase to be stabilized as deposited, resulting in inherent ferroelectricity. We further investigated the effect of the stack design, ALD process parameters, and post processing such as annealing on the ferroelectric properties of the HZO films in the capacitor. We report $2P_r$ values of nearly 30 μC/cm^2 under optimized conditions. Most significantly, we also observe that the coercive field can be reduced making the films more reliable under memory switching cycles. Coercive field tuning to values as low as ~1 MV/cm is demonstrated.

In summary, we have demonstrated inherently FE capacitors of HZO deposited by ALD of HfD-04 and ZrD-04 precursors where the FE properties can be tuned using the design of the capacitor stack, process conditions, and post process operations. Our work demonstrates how choice of Hf and Zr ligands and the widening of the ALD temperature window can enable a method of depositing FE films for on-chip memory application.

1:35pm **LI-ALD-TuM1-50 Ferroelectric Devices: From Applications to Microstructures***, **Asif Khan**,* Georgia Institute of Technology **INVITED**

The microelectronics industry is poised to enter the fourth wave of massive expansion, to support the explosion of Big Data and data-centric computing applications and the upcoming fourth industrial revolution. Ferroelectricity, standing on the remarkable streak of discoveries and innovations over the last 100 years, will be central to this new paradigm. In this talk, we will highlight the prospects and challenges of newly discovered fluorite-structure ferroelectrics (such as HfO_2 and its alloyed variants and ZrO_2) for advanced microelectronic applications [2]. The first part of the talk will focus on the application drivers of ferroelectric technologies such as embedded memories and ferroelectric neural networks [2,3]. The second part will describe the microscopic phenomena that underlies the macroscopic ferroic responses in fluorite-structure oxides as unveiled by a combination of multi-scale electron microscopy and first principles density functional theory-based calculations [4].

This research is supported by the National Science Foundation, the Defense Advanced Research Program Agency (DARPA), the Semiconductor Research Corporation (SRC) - Global Research Collaboration (GRC) program, the Applications and Systems-Driven Center for Energy-Efficient Integrated Nano Technologies (ASCENT), one of six centers in the Joint University Microelectronics Program (JUMP), a SRC program sponsored by the DARPA, and an Intel Rising Star award.

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1:55pm **LI-ALD-TuM1-54 Closing Remarks & Thank Yous***, **Tania Sandoval**,* Technical University Federico Santa Maria, Chile

We hope you enjoyed the session! We will see you tomorrow!

Live Session

Room Live - Session LI-ALD-TuM2

ALD Applications (AA) Live Session

Moderators: Prof. Annelies Delabie, IMEC, Prof. Jolien Dendooven, Ghent University, Belgium, Prof. Xiangbo Meng, University of Arkansas

9:30am **LI-ALD-TuM2-1 Welcome, Thank Yous & Instructions***, **Jolien Dendooven,*** Ghent University, Belgium

Thank you for attending and we hope you will enjoy the session!

9:35am **LI-ALD-TuM2-2 ALD Growth of Low Work Function Metal Gate for FinFET Technology***, **Jinjuan Xiang**, C. Zhao,* Institute of Microelectronics, Chinese Academy of Sciences, China*; Y. Ding,* Chemical and Material Engineering, Jiangnan University, China*; C. Xu,* Nata Opto-electronic Material Co., Ltd., China*; L. Du,* Chemical and Material Engineering, Jiangnan University, China*; J. Li, X. Wang,* Institute of Microelectronics, Chinese Academy of Sciences, China **INVITED**

As the feature size of CMOS device shrinks to 22 nm technology node, Fin field-effect-transistor (FinFET) structure with higher aspect ratio is introduced, resulting in difficulty for conformal deposition of gate stack on the 3D channel surface. Atomic layer deposition (ALD) is considered as the best way to conquer the above challenge. Plasma enhanced ALD of low work function metal has been studied for the N-type metal. The plasma during the ALD deposition might bring damage to the underlying dielectric, which might lead degradation to the device performance. Our works developed a thermal ALD method of growing low work function metal TiAlC and TaAlC without plasma. The lowest effective work function can be 4.24 eV. In this paper, thermal ALD of Al-containing alloys TiAlC and TaAlC are systematically investigated, including the deposition conditions, the material properties of the resultant metal and the effective work functions. It is demonstrated that the thermal ALD TiAlC or TaAlC films are promising gate metal candidates for FinFET device of 14nm technology node and beyond.

9:55am **LI-ALD-TuM2-6 Atomic Layer Deposition of GeTe/Sb$_2$Te$_3$ Superlattice for Large-Capacity and Low-Power Phase Change Memory***, **Chanyoung Yoo**, E. Park, W. Kim, J. Jeon, W. Choi, B. Park, G. Han,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

Despite the extensive research and available commercial memory products based on the phase-change-material (PCM), the advantages of Ge-Sb-Te alloy PCM for high-density and low-power memories have not been fully accomplished. This is primarily due to the current PCM architecture that relies on cross-point (X-point) arrays. The X-point cannot keep up with the ultra-high density demands of low cost per bit due to the increased fabrication cost by the lithography steps and masks required for each stacking layer. It can be best solved with the state-of-the-art vertical architecture, which is a proven technology with more than 150 layer stacks in V-NAND technology. To fabricate highly integrated vertical crossbar array (V-CBA) memory, the Ge-Sb-Te phase change layer should be deposited conformally on the etched sidewalls in this vertical architecture, and thus, Atomic Layer Deposition (ALD) technique is essential. Meanwhile, the high power consumption of the Ge-Sb-Te PCM during the writing operation is also a remaining challenge. Simpson et al.[1] suggested a GeTe/Sb$_2$Te$_3$ superlattice material as a substitute to solve such an issue. They argued that resistance change could be achieved with a lower current by flipping the Ge atom between octahedral sites and lower-coordination sites at the superlattice layers' interface.

This work demonstrates the development GeTe/Sb$_2$Te$_3$ superlattice film utilizing ALD to achieve high-performance V-CBA memory devices. The GeTe/Sb$_2$Te$_3$ superlattice thin film was successfully deposited as in Figures 1 and 2, where the out-of-plane directions of the two-component layers precisely matched the c-axis, while the in-plane directions were random. The superlattice films showed seven times (Figure 3) lower RESET than the conventional Ge$_2$Sb$_2$Te$_5$ alloy films, with the mushroom memory cell configuration. The reduction of RESET current with the alignment of the GeTe/Sb$_2$Te$_3$ superlattice films was also feasible in the vertical structure, showing the potential of the current process for the V-CBA memory of the GeTe/Sb$_2$Te$_3$ superlattice.

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10:10am **LI-ALD-TuM2-9 Atomic Layer Deposited p-type SnO Thin Films with c-axis Preferred Orientation and the Associated Device Applications***, **Hye-mi Kim**, S. Choi, H. Jeong, J. Park,* Hanyang University, Korea

Tin monoxide (SnO) films were fabricated by atomic layer deposition method using a N,N′-tert-butyl-1,1-dimethylethylenediamine stannylene (II) and deionized (DI) water as a precursor and reactant, respectively. In this study, we investigated film properties of SnO by annealing temperature with the focus on the relation of the crystal structure and phase transition with electrical characteristics. As annealing temperature was increased, phase transition occurred from SnO to SnO$_2$. Based on the experimental results such as the band gap, crystal structure, film composition, band structure, we conclude that 300℃ is optimized temperature in film properties which shows preferential growth in (001) plane. The highest hall mobility is observed (5.01 cm^2/Vs) at the 300℃ annealed temperature which may results from the reported low effective hole mass (m_h^*) along the [001] direction. Also, 400℃ is critical temperature for considering that the phase transition starts at the temperature from SnO to SnO$_2$. SnO channel based staggered bottom gate structure TFTs were fabricated and nitrogen annealing was followed. SnO TFTs showed p-type switching performance, when the device is exposed to the annealing condition of 300℃, in terms of threshold voltage (5.1±0.5 V and 1.7±0.4 V), field-effect mobility (6.0±0.0 cm^2/Vs and 4.9±0.2 cm^2/Vs), sub-threshold swing (4.6±0.2 V/decade and 4.4±0.2 V/decade) with high on-current/off-current ratio (2.7 x 10^2 and 2.5 x 10^2), at drain voltage is -0.1 V and -10.1 V, respectively. Also, threshold voltage shift was obtained during positive bias stress (+2.5 V) and negative bias stress (-7.7 V) at drain voltage is -10.1 V and gate bias stress is ±10 V. Additionally, observed conducting or degraded transfer curves in other annealing conditions indicates that understanding the film properties by annealing sequence leads to achieve improved p-type TFT fabrications.

10:25am **LI-ALD-TuM2-12 Atomic Layer Deposition of Highly Conductive Co$_9$S$_8$ Thin Films Using Diamine Adducts of Cobalt(II) Halides and H$_2$S***, **Miika Mattinen**,* Eindhoven University of Technology, Netherlands*; T. Hatanpää, K. Mizohata, J. Räisänen, M. Leskelä, M. Ritala,* University of Helsinki, Finland

ALD of metal sulfides has enjoyed a renaissance in the past decade, with some tens of new processes and 17 new binary sulfides reported since 2010.[1] Many of the processes deposit semiconducting sulfides such as MoS$_2$, SnS$_2$, and ZnS. However, for a multitude of applications, high electrical conductivity and/or metallic behavior are preferred. Cobalt pentlandite, Co$_9$S$_8$, is a highly conductive sulfide material that has shown promise as an electrode in a variety of energy applications ranging from water splitting to rechargeable batteries, supercapacitors, and solar cell electrodes. So far, only one ALD process using an expensive cobalt amidinate precursor has been reported in the literature, which results in films with a rather high resistivity of 3–5 mΩcm.[2]

We have developed a new Co$_9$S$_8$ ALD process using a recently reported[3] CoCl$_2$(TMEDA) (TMEDA = *N,N,N`,N`*-tetramethylethylenediamine) precursor with H$_2$S at 180–275 °C. The highest growth rate (~0.6 Å/cycle) and best film properties including the lowest amount of impurities (~3% total) and resistivity (ρ ≈ 70 μΩcm) are achieved at 275 °C. We have also evaluated a variety of similar cobalt precursors with different halide and diamine adduct ligands that exhibit adequate thermal properties as ALD precursors and afford Co$_9$S$_8$ growth with H$_2$S. All of these precursors can be easily synthesized using inexpensive starting materials.

The CoCl$_2$(TMEDA) + H$_2$S process enables growth of conductive films as thin as approximately 3 nm on silicon with native oxide. The process is also inherently selective, such that at least a 5 nm thick film can be grown on native silicon oxide with negligible growth on Si-H. Besides SiO$_2$, films can be grown on a range of substrates. We have also deposited the first epitaxial Co$_9$S$_8$ films in the literature using a hexagonal (0001)GaN substrate. The deposited Co$_9$S$_8$ films exhibit excellent thermal stability under a N$_2$ atmosphere up to at least 750 °C. The ability to deposit thin, continuous, highly conductive, and thermally stable Co$_9$S$_8$ films suggests that our process may be interesting for metal barrier and seed layer as well for various energy applications.

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10:50am **LI-ALD-TuM2-17 ALD-Oxide Materials and Surface Modification for Next-Generation PV Devices***, **Nathanaelle Schneider,*** Institut Photovoltaïque d'Ile de France **INVITED**

Zinc oxide is an extensively studied n-type semiconductor for various applications such as light emitting devices, detection of chemicals or solar cells, which often needs to be doped, modified or protected.

Doped-ZnO films can replace conventional transparent conductive oxides (TCO), especially in high aspect ratio structures. Silicon nanowire (Si NW) solar cells are interesting PV technology but challenging to contact.[1] Use of ALD-Ti:ZnO (TZO) as the top electrode for Si NW solar cells has proven the applicability of ALD-TZO as TCO and the unique capabilities of ALD, showing superior optoelectrical properties, conformally covering the Si NWs, and yielding a PV diode behavior with external quantum efficiency response surpassing ITO.[2]

In other cases, it can be beneficial to modify the properties of the ZnO surface by the grafting of organic molecules.[3] ALD-ZnO surfaces were modified by phosphonic acid derivatives with different spacer and functionalizing groups (2-AEPA, 4-ABzPA and 4-FBzPA), characterized, used to passivate the reactive ZnO/perovskite interface and solar cell devices were prepared.[4]

Finally, ZnO-based films often need to be protected to prevent their degradation. Al:ZnO (AZO) window layer is reported as the primary component responsible for the degradation of CIGS solar cells. The feasibility to prevent AZO degradation and encapsulate module-level (10×10 cm²) CIGS solar devices by a 10 nm ALD-Al_2O_3 barrier layer was demonstrated.[5] However, solar panels in field operation are also exposed to various chemical air pollutants such as in $(NH_4)_2SO_4$ in rural, and NaCl in marine environments. Their effects were studied by placing AZO w/ and w/o encapsulation in specific climatic test conditions. This demonstrated the necessity to consider atmospheric chemistry when evaluating barrier protection capacities of encapsulants and assessing the durability of PV materials and devices.[6]

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11:10am **LI-ALD-TuM2-21 Particle Atomic Layer Deposition as an Effective Way to Enhance the Li-S Battery Energy Density***, **Mato Knez**, S. Garcia,* CIC nanoGUNE, Spain

Lithium-sulfur (Li-S) batteries are the most promising candidates for succeeding lithium ion batteries. However, there exist some challenges which should be faced to increase its commercial possibilities. Those include detrimental mechanisms during operation (*e.g.* shuttle effect, low capacity retention, anode corrosion, *etc.*) and sulfur cathode processing limitations (*e.g.* poor mechanical stability of S cathodes, defects, low S loading, *etc.*).

From the industrial perspective, sulfur cathode manufacturing should be improved as uniform and highly sulfur-loaded cathodes are required in order to ensure energy densities above 400 $Wh \cdot kg^{-1}$, to become commercially competitive. The sulfur cathode manufacturing limitations are related to solvent evaporation upon drying, which commonly results in a significant cathode volume reduction. It provokes the formation of cracks and pores in the cathode, which negatively affect the electrochemical performance of the cell. This issue has been addressed by several strategies, including *(i)* varying the binder nature and content, *(ii)* gluing microporous nanoparticles into secondary particles of few microns, and *(iii)* introducing conductive polymers. Even immobilizers and physically confining structures have been developed, but in most of the cases, those materials tend to significantly increase the weight and volume of the cathode, thereby reducing the energy density of the Li-S battery.

Atomic layer deposition (ALD) with alumina (Al_2O_3) has been applied to sulfur cathode surfaces to improve the electrochemical behavior of Li-S technology as it minimizes discharge product dissolution and hence, it reduces detrimental mechanisms during operation. However, the improvement of sulfur cathode processing remains unsolved. Even high-cost approaches have been proposed in the state-of-the-art which unfortunately are not viable for realistic applications. In this work, for first time atomic layer deposition (ALD) in a fluidized bed reactor (FBR) is carried out to coat sulfur-carbon (S/C) composite particles with Al_2O_3 prior to electrode manufacturing. The present approach provides a precise control of S/C composite agglomeration, which improves sulfur cathode processing while maintaining the well-known satisfactory operational mechanisms related to Al_2O_3 coating. We report on the FBR-ALD technique as a promising strategy for fabricating high specific energy density Li-S batteries with an increased sulfur loading, being double of that obtained for a standard sulfur cathode (3.6 vs. 1.8 mg_{sulfur} cm^{-2}).

11:25am **LI-ALD-TuM2-24 Advanced ALD Technologies Platform to Enable Future Applications and Scaling & Review of Emerging Applications for Sensors, Mems, Energy Harvesters, Transparent Electronics and Coated Powder for Composites***, **Noureddine Adjeroud,*** Luxembourg Institute of Science and Technology (LIST), Luxembourg

The Luxembourg Institute of Science and Technology (LIST) proposes a large atomic layer deposition (ALD) platform with complementary tools for the development of new coating processes and the improvement of existing ALD processes. The platform allows processing of various types of inorganic or organic substrates, flat or 3D objects, flexible substrates and powders by FBR (Fluidized Bed Reactor) with up-scaling capabilities. The ALD platform is completed by other thin film deposition facilities, by cleanroom microfabrication capabilities to realize functional chips, and by a characterization platform (SEM-EDS, ellipsometry, contact angle, XRD, XPS, SIMS, AFM, UV-Vis-NIR spectrophotometry, Raman, photoluminescence, I(V), Resistivity) for quality control of the deposited thin films. This abstract is aiming to present ALD activities of our Technologies Platform covering the requests and specifications from fundamental research partners on breakthrough materials to the development and small production processing for industrial partners. A selection of ALD developments will be presented in the framework of LIST research and development projects addressing Lithium ion battery application (Co2O3), MEMS (MicroElectroMechanical Systems) and sensors (Figure 1), Energy Harvesters (Figure 2), Transparent Conducting Oxides such as ZnMgO, ZnSnO, ZnAlO, for transparent electronics (Figure 3), Example of Ag nano wires covered with conformal ALD ZnO film (Figure 4) and fillers' coating for composites (5). We are finishing a project that is looking at novel Aluminium nitride (AlN) film to be used in innovative energy harvesting applications, by the means of thermal ALD and Plasma-Enhanced ALD (PEALD). We developed a library of different thin films and multilayers processes including oxides (SnO, ZnO, TiO2, Al2O3, SiO2, MgO), nitride (AlN, TiN), metals (Ag, Co, Ni) (Figure 5) aiming both fundamental Research and applicative systems. Example of powder coating by FBR will be given (Figure 6).

11:40am **LI-ALD-TuM2-27 Molecular Layer Deposition of Li-Ion Conducting "Lithicone" Solid Electrolytes***, E. Kazyak, M. Shin, W. LePage, T. Cho, **Neil Dasgupta,*** University of Michigan, Ann Arbor

Atomic layer deposition (ALD) and its organic equivalent molecular layer deposition (MLD) have gained widespread attention as ultrathin functional materials in batteries, and have also been applied for interfacial coatings to stabilize electrode-electrolyte interfaces in battery systems. In particular, there is great interest in developing ALD/MLD films that are ionically-conductive and electronically insulating, which enables their use as solid electrolytes for either thin-film solid-state batteries or "artificial SEI" layers. MLD provides an important potential benefit over ALD films, due to improved mechanical compliance. MLD films are especially beneficial for interfacial coating of high-volume expansion electrodes and solid-state batteries. However, despite these promising characteristics, there have been only a few Li-containing MLD films reported to date, and no previous reports of ionic conductivity in MLD films.

In this work, we demonstrate the fabrication of Li-containing thin films ("lithicone") prepared via MLD, process using lithium *tert*-butoxide and ethylene glycol as precursors [1]. We demonstrate that the lithicone film grows in a self-limiting manner, using both spectroscopic ellipsometry and *in situ* quartz crystal microbalance (QCM) measurements. The evolution of the film morphology was revealed using glovebox-integrated atomic force microscopy (AFM) analysis, which eliminates artifacts from air exposure.

Glovebox-integrated X-ray photoelectron spectroscopy (XPS) measurements show that the bonding environment of lithicone films has C-O-Li moieties, which is distinct from that of lithium carbonate or alucone MLD films. To demonstrate the feasibility of using lithicone as a solid electrolyte or ionically conducting interlayer materials, the ionic conductivity of lithicone was measured systematically. The annealed lithicone film shows ionic conductivity of $3.6–5 \times 10^{-8}$S cm^{-1} with activation energy of ~0.6 eV. The measured electronic conductivity of the films was 5-6 orders of magnitude lower than the ionic conductivity, resulting in a transference number greater than 99.999%, and demonstrating that the lithicone films act as a solid electrolyte. This is the first quantified measurement of Li-ion conductivity in MLD thin film to-date, and will serve as a springboard to develop advanced organic/inorganic hybrid thin films for use in future battery applications.

[1] E. Kazyak, M. Shin, W. S. LePage, T. H. Cho, N. P. Dasgupta, *Chem. Commun.* **56**, 15537 (2020)

11:55am **LI-ALD-TuM2-30 Atomic-Level Precision at Large Scale: Opportunities and Challenges of ALD***, **Fatemeh Hashemi**,* TNO Science and Industry, the Netherlands **INVITED**

Atomic layer deposition (ALD) is a well-established method for the deposition of a variety of materials at a large scale and in industrial processing. While there are ever-growing efforts in the ALD community on the development of deposition materials with new properties and employing new chemistries, the well-developed processes have been scaled-up through innovative equipment designs, advanced precursor chemistries, and deposition methods.

In this talk, I will highlight some of the applications of ALD at large-scale including semiconductor electronics, powder coating, and photovoltaics (PV) manufacturing. I will focus on some basic concepts regarding the different design configurations and equipment that allow performing these processes and how the fundamental lab-scale studies in these areas have helped with accelerating the large-scale thin film deposition. To better understand the opportunities and challenges of ALD in these areas, I will discuss three specific studies including concepts related to area-selective ALD (AS-ALD) of metal oxides, nanoparticle deposition, and metal oxide barrier coating for solar cells.

First, I will highlight the advantages that the AS-ALD process brings to the large-scale fabrication of semiconductor electronics, recent efforts in the lab-scale focusing on metal-oxide deposition via ALD and the limitations that the field is facing. I will then briefly highlight the powder coating technology and what ALD can bring to the game, the state of the art, and the limitations. Lastly, I will show some examples of metal-oxides ALD as barrier or passivating layers in PV, specifically thin-film silicon solar cells, and how a combination of smart ALD process design with other state-of-the-art large-scale thin-film deposition techniques such as pulsed laser deposition (PLD) can result in high surface passivation and improved efficiency for silicon solar cells at large-scale. One example that I will focus on is the case of alumina ALD development for thin film PV which gave a boost to the PERC technology (Passivated Emitter Rear Cell) and opened up the industrial potential of ALD in PV.

12:30pm **LI-ALD-TuM2-37 ALD in Photovoltaics: From Extremely Thin to Ultrathin Layers, Physical Insight, and Chemical Methods Development***, P. Büttner, D. Döhler, Y. Cao, V. Koch, F. Scheler,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; C. Pointer,* Lehigh University*; S. Korenko, M. Barr, I. Mínguez-Bacho,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; E. Young,* lehigh University*; **Julien Bachmann**,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany **INVITED**

Atomic layer deposition (ALD) is ideally suited to the generation of ‘extremely thin absorber’ (ETA) solar cells, in which three distinct semiconductors are combined as electron transport layer (SnO_2, TiO_2, ZnO), light absorption layer (Sb_2S_3, Sb_2Se_3), and hole transport layer (V_2O_5 or spin-coated organics).

We have used ALD to explore and optimize individual geometric parameters of planar and nanostructured ETA cells. In the planar case, the compromise between light absorption and charge collection in Sb_2S_3 yields 60 nm as the optimal light absorber thickness. An underlying ZnS layer serves to improve adhesion between Sb_2S_3 and the oxide, and behaves as a tunnel barrier. Here, the ideal thickness that best balances an efficient direct electron transfer with a blocked recombination lies at 1.0 nm.

This materials system can also be implemented in parallel arrays of coaxial, cylindrical p-i-n heterojunctions. In that situation, the cylinder length that maximizes the overall solar energy conversion efficiency is 750 nm. Dewetting of heavy chalcogenides becomes an issue in such geometries that feature strongly curved surfaces. It can be prevented by a sacrificial ZnO layer that is removed after annealing. In that procedure, we find that an undesired barrier to charge transfer is formed due to redox chemistry at the interface. However, the formation of this barrier can be prevented by carefully oxidizing the surface of Sb_2S_3preliminary step. This trick even allows for the conformal coating of nanospheres, and the generation of solar cells based on nanosphere monolayers that feature interesting photonic effects.

Similarly structured coaxial p-i-n heterojunctions cannot be generated with hybrid perovskites as the light absorber, given that the ionic nature of perovskites renders them inaccessible from gaseous precursors. For this purpose, we have developed ALD from precursors in solution, or sALD. This new method yields high-quality semiconductors, even crystalline ones, at or near room temperature.

Taken together, these results demonstrate the power and versatility of ALD to control and engineer each layer of a photovoltaic stack, but also each interface between them, down to the level of individual atoms.

12:50pm **LI-ALD-TuM2-41 Demonstration of Pt-Wire Temperature Sensors Fabricated by Atomic-Layer 3D Printer Using $MeCpPtMe_3$ and O_3***, **Gabriel Vanko**, B. Hudec,* Slovak Academy of Sciences, Slovakia*; M. Precner,* Institute of Electrical Engineering, Slovak Academy of Sciences, Bratislava, Slovakia*; I. Kundrata, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany*; K. Fröhlich,* Slovak Academy of Sciences, Slovakia

This case study demonstrates Pt-wire temperature sensors fabricated by a rapid prototyping atomic-layer 3D printer utilizing a combination of ALD, microfluidics and high precision 3D printing [1], first time introduced at AVS ALD 2020 [2].

The printer nozzle moves relative to the substrate in a highly controlled manner (in this case ~2 mm/s) following a pre-programmed pattern. The nozzle is a miniature spatial ALD system where the precursor ($MeCpPtMe_3$ in this case) flows out of the center of the nozzle, surrounded by a concentric rings of vacuum and a reactant gas (O_3). The result is an area-selective ALD of pre-programmed patterns, where each nozzle pass over the substrate equals to one ALD cycle.

In this demonstration, >2 mm long Pt-wires of different thicknesses were printed using 100-500 ALD cycles at 200, 225 and 250 °C, where the width of the wires (~400 µm) was defined by the used nozzle geometry.

Morphology studies of the Pt surface by scanning electron microscopy revealed the island-like growth mechanism, typical for this thermal ALD Pt process [4], as well as certain effects on the wire edges, discussed in detail in [3].

The sensor was annealed for 30 min at 600 °C in N_2 atmosphere as a first step to ensure thermal stability. The wires’ ends were capped by Au contact pads 2 mm apart (using e-beam PVD through a shadow mask) and measured electrically for their temperature sensor characteristics in the 25-400 °C range, as well as in cryogenic temperatures down to 3 K.

Interestingly, higher temperature sensitivity *S* was found for samples made by 200 ALD cycles, with a morphology of a network of interconnected Pt grains.

The comparison of temperature coefficient of resistivity α (normalized sensitivity) clearly shown that the printed ALD Pt demonstrate better temperature sensing characteristics than the conventional 30 nm e-beam PVD Pt thin film, and is comparable also to the Pt100 standard.

We will also discuss sensors printed on corrugated surfaces, i.e. black Si and Si gratings.

Online suppl. figures show the fabrication flow, SEM micrographs and electrical properties. The authors acknowledge the support of the H2020-EU ATOPLOT project (grant ID: 950785).

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1:05pm **LI-ALD-TuM2-44 Optimization of 1D Core-Shell Heterostructures for Gas Sensing***, M. Raza,* ***Nicola Pinna****,* Humboldt University Berlin, Germany

Hierarchical core-shell heterostructures composed of p- and n-type metal oxide shells deposited onto carbon nanotubes (CNTs) were synthesized using atomic layer deposition. Precisely controlled films of alternating metal oxides were uniformly deposited onto the inner and outer walls of the CNTs. The morphological, microstructural and electrical characteristics of the as prepared core-shell heterostructures were thoroughly investigated. The electrical resistance measurements highlighted the large influence of the metal oxides thickness and charge carriers types on increasing of many order of magnitude the baseline resistance of the core-shell heterostructures with various thicknesses of the metal oxide shell layers, suggesting that the conductivity of the sensors is dominated by Schottky barrier junctions across the n-p interfaces.

The behavior of our sensors was investigated for low concentrations of volatile organic compounds and pollutants. The gas sensing response of the heterostructures showed a strong dependence on the thickness of the metal oxide shell layers and the type of heterostructures formed. On the basis of the morphological, microstructural and electrical characterization and sensing results, the sensing mechanism which accounts for the marked variation in the resistance during the interaction of the target gas molecules will be discussed.

1:20pm **LI-ALD-TuM2-47 Bridging the Synthesis Gap in Vapor-Phase Deposition using Ionic Liquid as Solvent***,* ***Jingwei Shi****, S. Bent,* Stanford University

Molecular layer deposition (MLD) is a vapor-phase organic thin film deposition method useful for applications such as photolithography, lithium batteries, and microelectronics. However, while MLD offers excellent control over thickness and conformality, there is a more limited range of possible film chemistries compared to wet deposition techniques. We introduce a modified MLD technique, termed ionic liquid assisted MLD (IL-MLD) to overcome these limitations. The surface reactions of an IL-MLD process are performed inside an ultrathin layer of a suitable ionic liquid (IL) to replicate solvent effects inside a vacuum system, widening the number of possible chemical reactions used. The IL-MLD of polyetherketoneketone, an industrially and research-relevant, high performance thermoplastic, is demonstrated with this technique. By this proof-of-concept, we show that IL-MLD can enable the synthesis of ultra-thin polymeric films via solvent-mediated reactions which may be adapted to other vapor deposition techniques as well.

1:35pm **LI-ALD-TuM2-50 A Model of ALD Particle Coating in Fluidized Bed Reactors: Comparison With Experiments and Other Particle Coating Techniques***,* ***Angel Yanguas-Gil****, Z. Lu, P. Darapaneni, D. Kang, A. Mane, J. Kropf, C. Marshall, J. Elam,* Argonne National Laboratory

The ability to efficiently coat large batches of particles by atomic layer deposition is crucial for applications such as energy storage and catalysis. In recent years, fluidized bed reactors have shown strong promise as a pathway towards scale up of ALD in particles. In this work, we present a model of ALD in fluidized bed reactors. Using some fundamental approximations, we reduce the model to a set of analytic expressions that provide the time evolution of surface coverage inside the reactor as well as of precursor and byproduct species in the downstream area, using fundamental process and reactor parameters as inputs. A comparison between the model and experimental results on the ALD of Al_2O_3 using TMA and water in a commercial fluidized bed tool shows that the model is able to capture the main behaviors experimentally observed using in-situ mass spectrometry.

We then use this model to explore and compare the scale up of particle coating using fluidized bed reactors, rotating drum reactors both under constant flow and static dose conditions, and spatial ALD approaches using particle agitation, all methods that have been explored in the literature. The results obtained provide upper boundaries for dose times (throughput) and precursor utilization based on fundamental aspects of the precursor-surface interaction, such as the growth per cycle or the initial reaction or sticking probability, the maximum mass rates achievable for ALD precursors, and the volume and surface area of the particles. The resulting models can be used to explore the integration of ALD particle coating into more complex process flows.

1:50pm **LI-ALD-TuM2-53 Closing Remarks & Thank Yous***, X. Meng,* University of Arkansas

We hope you enjoyed the session! We will see you tomorrow!

Live Session

Room Live - Session LI-ALE-TuM3

Atomic Layer Etching Live Session I

Moderators: Prof. Gottlieb Oehrlein, University of Maryland, Dr. Dmitry Suyatin, Lund University

9:30am **LI-ALE-TuM3-1 Welcome, Thank Yous, & Instructions***, **Dmitry Suyatin,*** Lund University, Sweden*; G. Oehrlein,* University of Maryland

Welcome to the session! We hope you will enjoy the it!

9:35am **LI-ALE-TuM3-2 Atomic Scale Profile Control in Fine Pitch Patterning and High Aspect Ratio Contact Hole Etching***, **Tetsuya Nishizuka,** S. Kumakura, T. Katsunuma, Y. Kihara, M. Honda,* Tokyo Electron Miyagi, Ltd., Japan **INVITED**

In recent semiconductor device manufacturing processes, high aspect ratio contact hole etch has been the most challenging one. As the aspect ratio (AR) increases along with smaller critical dimension (CD) and vertically stacked 3D device structure, satisfying both vertical profile and selectivity to mask layer is getting harder. Especially “bow” profile which is caused by side etch generated under the mask is the top issue to address. Conventional approach to mitigate those problem is optimizing etching conditions such as gas chemistry or radio frequency (RF) power in accordance with the depth. Namely that controls radical species of etch/deposition balance and ion energy. However, since the deposition in this case is a kind of PECVD, its low step coverage characteristic causes clogging at the opening of mask and lack of thickness for sidewall protection in high AR structure. An alternate approach is separating etching and deposition steps, and cycling them. In this way, ALD can be applied as the deposition step. ALD’s conformal coverage and atomic level controllability enable sufficient sidewall protection, and avoid clogging. Recently some results show a potential of excellent profile controllability which was impossible by conventional approach [1, 2]. Whereas in terms of bow improvement, even ALD is not always ideal because sidewall protection is necessary at only shallow area of contact hole while the bottom area and mask opening need to keep CD as wide as possible. This time we developed more ideal coverage ALD technique by utilizing under-saturation region and optimizing gas condition in the activation step. By combining this novel sidewall protection technique and etching reaction, more flexible etching process for high AR structure is realized.

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9:55am **LI-ALE-TuM3-6 Nanoscale Cryogenic Process for Highly Selective Etch of Si_3N_4 Over Si***, **Gaelle Antoun,** T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; A. Girard,* IMN CNRS/Université de Nantes, France*; C. Cardinaud,* IMN CNRS/Université d'Orléans, France*; J. Faguet,* Tokyo Electron America Inc.,*; K. Maekawa, D. Zhang, H. Kim, M. Wang,* TEL Technology Center, America, LLC*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

In 1988, Tachi *et al.* developed a cryogenic process using SF_6 plasma in order to etch Si anisotropically [1]. Since, many other studies were conducted in order to understand the mechanisms involved in cryo-etching. It was shown that oxygen is needed to build a passivation layer on the trench sidewalls [2]. This passivation layer can only be formed at low temperature and is desorbed once brought back to room temperature. Cryogenic processes present several advantages such as the limitation of material damage and reactor wall contamination [3].

In a previous work, we proposed an SiO_2 cryo-ALE process based on the physisorption of C_4F_8 during the modification step. However, this process was only demonstrated for temperatures between -120°C and -90°C [4] and selectivity to Si and Si_3N_4 was limited.

In this work, a different approach is proposed at low temperature (between -100°C and -50°C) to perform highly selective nanoscale etching. It this process, the modification step consists in depositing in plasma phase a layer stable only at low temperature. The etching step is an Ar plasma with low ion bombardment energy.

A cryogenic ICP reactor has been used to carry out this work. An in-situ Spectroscopic Ellipsometer is coupled to this reactor in order to monitor the surface thickness evolution over time. Quasi in-situ XPS measurements have also been performed. The equipment is composed of an ICP reactor coupled to the XPS chamber. A coupon is fixed on a transfer rod that can be cooled with liquid nitrogen and biased. Therefore, once processed, the sample can be transferred to the analysis chamber while remaining at low temperature.

Tests were performed on Si_3N_4 and p-Si coupons glued on a SiO_2 6” carrier wafers.

First, the influence of the modification step on the two materials was investigated at different temperatures. The same study was repeated to perform XPS measurements and characterize the modified surface. At room temperature, the established process is in a deposition regime for both materials. However, at low temperature, it becomes possible to switch to an etching regime. It has been evidenced that the threshold temperature for switching from deposition to etching is different for each material. Therefore, it is possible to etch Si_3N_4 selectively to Si at nanoscale by tuning wisely the substrate temperature.

The authors thank S. Tahara for all the helpful discussions.

This work was supported by CERTeM 2020 platform, which provides most of the equipment.

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10:10am **LI-ALE-TuM3-9 Using Selective Surface Functionalization of SiN_x to Increase SiO_2 to SiN_x ALE Selectivity***, R. Gasvoda, **Xue Wang,*** Colorado School of Mines, USA*; P. Kumar, Z. Zhang, E. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines, USA

Atomic layer etching (ALE) and its derivatives can provide high etch fidelity, atomic–scale precision, directionality, and high selectivity that is required for manufacturing of sub–7–nm node semiconductor devices. Specifically, ultra–high etch selectivity for SiO_2 vs. SiN_x is required in the manufacturing sequence, especially in the self–aligned contact etch approach. Plasma–assisted ALE of SiO_2 typically consists of two sequential half–cycles: fluorocarbon (CF_x) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Generally, ALE process parameters can be tuned to maximize overall SiO_2 vs SiN_x etch selectivity (similar to continuous etching). Recently, we have identified a novel approach to enhance the etch selectivity by selectively pre–functionalizing the SiN_x surface to protect against the etch process.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy in combination with *in situ* 4–wavelength ellipsometry to monitor surface reactions, film composition as well as etch per cycle during ALE. Further, the ion energy distribution (IED) in the Ar plasma activation half–cycle is characterized with a retarding field energy analyzer. We have previously demonstrated that aldehydes can be used to selectively functionalize SiN_x from the gas phase without plasma, with minimal effect on SiO_2. In particular, benzaldehyde selectively functionalizes only the SiN_x surface with sp^2–hybridized–carbon (see Fig. 1a and 1b). We show that the overall SiO_2:SiN_x etch selectivity for a target SiO_2 etch of ~15 nm can be increased from ~2.1 to 4.5 simply by pre–functionalizing the SiN_x surface with benzaldehyde prior to beginning ALE (see Fig. 2a). Additionally, the infrared spectrum of the benzaldehyde functionalized SiN_x surface post etch shows more graphitic hydrofluorocarbon film accumulation than the infrared spectrum of the bare SiN_x surface, indicating that the added sp^2–hybridized–carbon from benzaldehyde remains on the surface leading to a reduction in the overall etch (see Fig 2b). We will also discuss various re–functionalization sequences in order to further maximize the overall SiO_2:SiN_x etch selectivity. Further, we discuss the effect of maximum ion energy and IEDs in the activation step on overall etch selectivity with specific focus on non–ideal Ar plasma activation steps where the maximum ion energy is above the sputtering threshold of both SiO_2 and SiN_x.

10:25am **LI-ALE-TuM3-12 Etch-stop Mechanisms in Plasma-assisted Atomic Layer Etching of Silicon Nitride: A Molecular Dynamics Study***, **Jomar Tercero,*** University of the Philippines*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; M. Vasquez, Jr.,* University of the Philippines*; S. Hamaguchi,* Osaka University, Japan

Plasma etching is one of the most technically demanding processes used in the fabrication of advanced semiconductor devices. Recently atomic-scale control of etching processes has become a topic of wide interest, following the urgent needs in developing manufacturing technologies for nano-meter-scale devices in the modern semiconductor industry [1-3]. To achieve atomic-scale control of etching processes, a better understanding of surface reaction mechanisms of the existing etching processes is the first key step. In earlier experiments, the etch stop in atomic layer etching (ALE) processes of silicon nitride (Si_3N_4) was observed after several ALE cycles [4]. The goal of this study is to find the reason for this etch stop. In a typical ALE process, a cycle of the surface modification step and the removal step of the modified layer is repeated. In the ALE process mentioned above, a hydrofluorocarbon (HFC) layer is deposited on a Si_3N_4 surface in the surface modification step, and then the surface is exposed to low-energy Ar^+ ion bombardment in the removal step. In this study, molecular dynamics (MD) simulations were used to emulate the ALE processes. The simulations have shown that, during the removal step, the Si_3N_4 etching is enhanced by chemical reactions with HFC atoms but a large amount of carbon typically remains on the surface after the removal step. The carbon remnants increase the sticking probability of HFC radicals in the subsequent surface modification step and induce thicker HFC deposition, which leads to the etch stop eventually after a few cycles. The validity of the simulations was tested by comparing the simulation results with available experimental observations.

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10:50am **LI-ALE-TuM3-17 Landscape of Spontaneous Etch via Ligand-Exchange in Thermal Atomic Layer Etching***, **Ann Lii-Rosales**, A. Cavanagh, S. George,* University of Colorado Boulder **INVITED**

Thermal atomic layer etching (ALE) utilizes sequential, self-limiting surface reactions to remove materials on the atomic level. Thermal ALE consists of two steps: (A) surface modification and (B) removal via volatilization. For metal oxide thermal ALE, surface modification usually involves fluorination using HF.[1] This fluorination creates a surface layer of metal fluoride. A strategy for volatilization can use ligand-exchange reactions. The exchange of F for Cl is an effective pathway, because metal chlorides are generally more volatile than the corresponding fluorides.[1] The resulting metal chloride can be thermally desorbed from the surface, leading to metal removal.

Both A and B steps are necessary for thermal ALE. However, material removal is achieved only by ligand-exchange. This renders the B step crucial for determining a metal's propensity for etching. Hence, a pre-fluorinated surface can be used as a model surface, which assumes the form of the fluorinated metal surface. One can use ligand-exchange reactions with the model fluorinated surface as an indicator for spontaneous etch.

A new reactor was constructed to probe the ligand-exchange reaction. The reactor uses *in situ* quadrupole mass spectrometry (QMS) to detect gas-phase products generated during ligand-exchange. Metal fluoride powders were used as model surfaces. Precursors for ligand-exchange were flowed through the powder over a wide temperature range, while gas-phase products were monitored by QMS in real time. This new reactor is unique in that the etch products are entrained in a molecular beam that has line-of-sight to the QMS ionizer. This configuration enables direct and accurate analysis.

The landscape for ligand-exchange reactions turned out to be unexpectedly rich. By surveying a variety of systems, the landscape can be categorized as the follow: (1) Ligand-exchange and volatile etch products occur at similar temperature; (2) Ligand-exchange happens at low temperature, but etch products do not desorb until high temperature; and (3) ligand-exchange happens, but there are no etch products. Representative systems are AlF_3 + $Al(CH_3)_3$ and SnF_4 + $TiCl_4$ for category (1), HfF_4 + $SiCl_4$ and InF_3 + $SiCl_4$ for category (2), and AlF_3 + $SiCl_4$ for category (3). The categories can be visualized from the intensity traces of precursor vs. etch product as a function of temperature. The new QMS reactor revealed the complexity of ligand-exchange and showed that the spontaneous etch systems can serve as predictors for thermal ALE of new materials.

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11:10am **LI-ALE-TuM3-21 Mechanisms of Self-Limiting Processes in Thermal Atomic Layer Etching of Nickel by β-diketones***, **Abdulrahman Basher**, I. Hamada, T. Ito, K. Karahashi , S. Hamaguchi,* Osaka University, Japan

Thermal atomic layer etching (ALE) is one of the key manufacturing technologies for nano-scale electronic devices [1] as it can be used for precise and damageless etching of metals. The mechanisms of thermal ALE of Ni with hfacH were examined in detail in previous studies [2-4]. It starts with the deprotonation of hfacH molecules after oxidizing the Ni surface. By increasing the surface temperature in the range of 300 ~ 400 °C, volatile nickel complex $Ni(hfac)_2$ and water H_2O molecules are formed on the surface and remove the NiO layer. In this process, once a new metallic Ni surface appears, no further etching occurs, which ensures the self-liming nature of the thermal ALE process [3-5]. It has been known experimentally [5,6] that, when hfacH molecules are supplied to a metallic Ni surface, they decompose and form neither $Ni(hfac)_2$ nor H_2O molecules, and as a result no etching of Ni takes place. The origin of the self-limiting process in the thermal ALE of Ni with hfacH exposure was discussed in an earlier study[4]. The aim of this work is to clarify the mechanisms of decomposition of other β-diketones on a metallic Ni surface and the effect of surface roughness on the decomposition concerning thermal ALE. In this study, van der Waals inclusive [7] periodic DFT is employed to investigate the adsorption and reaction processes of β-diketones such as hfacH, tfacH, and acacH on flat and rough metallic Ni surfaces, using a STATE code [8]. It has been found that the physisorption energies of those β-diketones are almost the same while the chemisorption energy is higher for a β-diketone with a higher polarity and the van der Waals forces play a decisive role in determining the adsorption energy. The dissociation processes of β-diketones have been studied with a climbing image nudged elastic band method, which has shown the cleavage of a C-F bond of a β-diketone is more likely to take place than the deprotonation. The surface roughness can also help to form C-Ni bonds, which were also observed in experiments. In this way, our simulations have demonstrated the self-limiting nature of thermal ALE for Ni with β-diketone gases in general, which is consistent with earlier experimental observations [5,6].

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11:25am **LI-ALE-TuM3-24 Oxidation Influences Etch Quality in the Low-Temperature Thermal ALE of Copper***, **Martin McBriarty**, J. McWilliams, M. Moinpour, R. Kanjolia, K. Littau,* EMD Electronics

Low-temperature thermal atomic layer etching (ALE) of copper is an appealing approach to controlled isotropic removal of Cu for emerging middle- and back-end-of-line (MOL and BEOL) steps in semiconductor device manufacturing. Cu ALE can proceed by controlled oxidation of the Cu surface followed by the volatilization of copper oxide. The isotropic removal of Cu with minimal surface roughening is critical for process integration, and a low-temperature process is necessary to avoid migration of highly mobile Cu to adjacent parts of the device or structure of interest. We investigated the plasma-free low-temperature oxidation of physical vapor deposited (PVD) Cu thin films by various oxidizing agents, as well as the subsequent volatilization of surface copper oxide by the beta-diketone hexafluoroacetylacetone (Hhfac). Depending on the oxidant and process conditions, we measure the removal of <0.5 Å to >5.0 Å of Cu per ALE cycle. We determine the influence of oxidation chemistry and kinetics on the etch behavior, surface chemistry, and film morphology, guiding the development of rapid, atomically precise, and selective low-temperature ALE processes for Cu.

11:40am **LI-ALE-TuM3-27 Thermal Atomic Layer Etching of Al_2O_3 and AlN Using HF or XeF_2 for Fluorination and BCl_3 for Ligand-Exchange***, **Austin Cano**, S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 and AlN can be performed using HF or XeF_2 as the fluorination reactant and BCl_3 as the ligand-exchange reactant. To investigate the etching mechanism, in-situ FTIR spectroscopy was used to identify the surface species and in-situ spectroscopic ellipsometry was employed to measure the etch rates. Quadrupole mass spectrometry was also employed to identify the volatile etch products. The Al_2O_3 studies were performed using Al_2O_3 ALD films grown using trimethylaluminum (TMA) and water as the reactants. The AlN investigations were conducted using crystalline AlN to explore the etch rates. The FTIR experiments employed AlN films grown by ALD using tris(dimethylamido)aluminum and ammonia as the reactants.

When BCl_3 is used as a reactant, the ALE mechanism could occur by BCl_3 conversion of Al_2O_3 to B_2O_3 or AlN to BN. Alternatively, BCl_3 could undergo ligand-exchange with the fluorinated AlF_3 surface. For thermal Al_2O_3 ALE, FTIR studies revealed strong evidence for a conversion reaction during the initial BCl_3 exposure on Al_2O_3. The original Al-O vibrational modes were converted to B-O vibrational modes by the initial BCl_3 exposures as shown in Figure 1. However, after the first ALE cycle using sequential HF and BCl_3 exposures, there was no more evidence of conversion and the Al_2O_3 etching proceeded through a fluorination and ligand-exchange mechanism. Quadrupole mass spectrometry measurements observed that BCl_3 exposures to AlF_3 yielded BCl_2F and $AlCl_3$ reaction products. In situ ellipsometry measurements determined that the Al_2O_3 ALE etch rate using HF and BCl_3 as the reactants varied with temperature from 0.01 Å/cycle at 270°C to 0.19 Å/cycle at 330°C.

In-situ FTIR and spectroscopic ellipsometry were also used to explore thermal AlN ALE. FTIR studies revealed that the initial BCl_3 exposures created a thin BN layer on the surface. Subsequent HF and BCl_3 exposures were consistent with AlN fluorination by HF and subsequent F/Cl exchange to form volatile $AlCl_3$ product during BCl_3 exposures. The Al-N vibrational stretch decreased progressively versus number of HF/BCl_3 cycles as displayed in Figure 2. HF was not able to fluorinate single crystalline AlN substrates. Consequently, XeF_2 was required as a stronger fluorination source. When combining viscous flow XeF_2 exposures with static BCl_3 exposures, ellipsometry measurements showed that AlN etching occurred at temperatures above 220°C. An etch rate of 0.81 Å/cycle was obtained at 255°C. In contrast, growth of a top layer that may be composed of AlF_xCl_y was observed at lower temperatures. This top layer could be removed by long static BCl_3 exposures.

11:55am **LI-ALE-TuM3-30 Closing Remarks & Thank Yous***, **Gottlieb Oehrlein,*** University of Maryland*; D. Suyatin,* Lund University, Sweden

Thank you for attending today's session. We will see you tomorrow!

Live Session
Room Live - Session LI-ALD-WeM1
Selective Deposition (AS) Live Session

Moderators: Prof. Adam Hock, Illinois Institute of Technology, Prof. Henrik Pedersen, Linköping University, Sweden, Prof. Matti Putkonen, University of Helsinki

9:30am **LI-ALD-WeM1-1 Welcome, Thank Yous & Instructions***, Matti Putkonen,* University of Helsinki, Finland

Thank you for attending today's session. We hope you will enjoy the session!

9:35am **LI-ALD-WeM1-2 Another Opportunity in Area Selective Atomic Layer Deposition using Precursor Inhibitors***, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea **INVITED**

Area-selective atomic layer deposition (AS-ALD) is envisioned to play a key role in next-generation nanofabrication for Si devices. Basics concept of AS-ALD is that an original surface is changed to activated or deactivated surfaces toward following ALD reactions, resulting in selective growth in one substrate. Although self-assembled monolayers (SAMs) have been successfully introduced for the change of surface properties and showed promising results in the early study of AS-ALD, they still have several disadvantages for high volume manufacturing (HVM), such as the low thermal stability and pattern interference from their inherent size. Several years ago, our research group has suggested that many ALD precursors could be used for an inhibitor of AS-ALD by utilizing their adsorption selectivity on surfaces and reaction selectivity with counter reactant. Because the inhibitor, itself, is a precursor, it has high compatibility in HVM and multifunctionality between the roles of inhibitor and precursor. In this presentation, various types of precursor inhibitors studied in our group will be summarized and another opportunity of our AS-ALD will be discussed. A combined process of AS-ALD and atomic layer etching (ALE) was studied by designing process sequence and combination of inhibitor and counter reactants. In addition, another concept of selective deposition by using a homogeneous precursor inhibitor was proposed for thickness control of ALD thin films inside 3D structures. The chemical and physical interactions of inhibitors with precursors were successfully explained through theoretical calculations by density functional theory (DFT)and Monte Carlo simulation. The results could provide insights for the next generation patterning process using ALD.

9:55am **LI-ALD-WeM1-6 Direct Deposition of High-resolution 3D Nanostructures by Atomic-Layer Additive Manufacturing (ALAM)***, **Sarah Tymek**,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; I. Kundrata,* ATLANT, Germany*; M. Barr,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; P. Wiesner,* ATLANT, Germany*; M. Plakhotnyuk,* ATLANT, Denmark*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Confining spatial ALD (atomic layer deposition) laterally to a spot with a size in the micron range allows one to perform ALD cycles by repeated passes of the deposition head above the substrate. The pattern defined by the motions of the deposition head may be arbitrarily complex. This concept allows for the definition of deposits in three dimensions in the manner of classical additive manufacturing (3D printing). However, the vertical resolution of the shapes generated is defined by the surface chemical principles of ALD, and therefore is on the order of single atoms. The lateral resolution depends on the printing head and the gas flows and is currently on the order of hundreds of µm.

We have demonstrated the self-limiting behavior of this atomic-layer additive manufacturing (ALAM) procedure for several materials. Under atmospheric conditions, the deposition of TiO_2 occurs with the same growth per pass as in conventional ALD. The cross-section of a deposit exhibits a horizontal surface and sharp edges. The self-limiting behavior of the surface chemistry is maintained. As an example of a noble metal, Pt grows in a highly crystalline and even oriented form. Air-sensitive precursors such as the metal alkyls can be handled safely in aerobic conditions, and the growth of Al_2O_3 and ZnO occurs with familiar characteristics.

Thus, ALAM is a novel method allowing for the direct generation of multimaterial structures without the need for preliminary or subsequent patterning. The combination of several materials in not only lateral juxtaposition but also vertical arrangement further enables one to use sacrificial deposits and generate complex three-dimensional structures.

10:10am **LI-ALD-WeM1-9 The Relation between Reactive Surface Sites and Precursor Choice for Area-Selective Atomic Layer Deposition***, **Marc Merkx**, A. Angelidis, J. Li,* Eindhoven University of Technology, Netherlands*; D. Hausmann,* Lam Research Corp.*; E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

Small and volatile molecules are of interest as alternative inhibitor for area-selective ALD to better meet the requirements for industrial processing.[1,2] However, due to their size and lack of surface ordering, it is much more challenging to achieve the high surface packing density that is required to block precursor adsorption through steric hinderance (i.e. physical shielding). In this work, we explore the central question whether area-selective ALD with high selectivity requires; (i) physical shielding through steric effects, (ii) chemical passivation by eliminating the reactive surface sites required for precursor adsorption, or (iii) a combination of both physical shielding and chemical passivation. At the same time, we investigate why some precursors are more difficult to block than others.

Precursor blocking was studied using *in-situ* infrared (IR) spectroscopy for trimethylaluminum (TMA), dimethylaluminum isopropoxide (DMAI), tris(dimethylamino)aluminum (TDMAA), and bis(diethylamino)silane (BDEAS) precursors using acetylacetone (Hacac) as inhibitor. It was found that TMA can adsorb on both isolated and H-bonded (i.e. vicinal) OH groups, whereas DMAI, TDMAA, BDEAS and the Hacac inhibitor only adsorb on isolated OH groups. Correspondingly, it was found that blocking TMA adsorption is much more challenging as compared to the other precursors. In addition, the IR spectra show a consumption of vicinal OH groups when dosing TMA on a Hacac-functionalized Al_2O_3 surface, which indicates that TMA can adsorb on the vicinal OH groups in between the Hacac inhibitor molecules. Taken together, it can be concluded that precursor blocking is more effective if the inhibitor and precursor adsorb on the same surface sites during area-selective ALD. To achieve this required overlap it is vital to carefully consider the choice of the precursor.

[1] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, A.J.M. Mackus, *ACS Nano***11**, 9303-9311 (2017).

[2] R. Khan, B. Shong, B.G. Ko, J.K. Lee, H. Lee, J.Y. Park, I.K. Oh, S.S. Raya, H.M. Hong, K.B. Chung, E.J. Luber, Y.S. Kim, C.H. Lee, W.H. Kim. H.B.R. Lee, *Chem. Matter.***30**, 7603-7610 (2018)

10:25am **LI-ALD-WeM1-12 Diffusion-Mediated Ruthenium Area-Selective Atomic Layer Deposition in Nanopatterns***, **Jan-Willem J Clerix**, E. Marques, J. Soethoudt,* KU Leuven / imec, Belgium*; F. Grillo,* ETH Zurich, Switzerland*; G. Pourtois,* imec, Belgium*; J. Van Ommen,* TU Delft, Netherlands*; A. Delabie,* KU Leuven / imec, Belgium

Area-selective deposition (ASD) opens up new avenues in the fabrication of next-generation nanoelectronic devices, as this bottom-up approach can complement conventional top-down lithographic patterning. However, a major challenge is defectivity due to the undesired growth of nanoparticles on the non-growth area. In this work, we model Ruthenium ASD by (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 Atomic Layer Deposition (ALD) with Kinetic Monte Carlo (KMC) methods to investigate the ASD mechanism on line-space nanopatterns with different dimensions. ASD is governed by adsorption as well as diffusion, and diffusion of Ru adatoms and nanoparticles from the non-growth to growth surface becomes more important when pattern dimensions decrease. A key feature of the Ru ALD process is the size-dependent mobility and reactivity of Ru nanoparticles. Nanoparticles that are too small to catalyze O_2 dissociation do not grow via precursor adsorption, but they diffuse and aggregate with each other or at the interface with the growth area. This results in nearly full depletion of Ru on the non-growth pattern for widths of 50 nm and smaller for a large number of cycles, as all Ru adspecies are captured at the growth interface before growth by adsorption is catalysed and before they become immobile. In addition, we observe a depletion zone near the interface with the growth area for patterns with larger dimensions. Overall, this mechanism results in smaller and fewer Ru nanoparticles on the non-growth surface, which is highly beneficial for etch-based defect mitigation (Figure 1). These predictions are supported by the experimental observation of reduced defectivity on the non-growth area near the interface with the growth area in nanoscale line-space patterns (Figure 2). We provide a promising outlook for defect mitigation for Ru ASD by passivation/deposition/etch cycles and for Ru ASD in nanopatterns with even smaller dimensions.

10:50am **LI-ALD-WeM1-17 Area-Selective CVD of Metallic Films on Oxide Substrates With Acidic or Basic Hydroxyl Groups***, **Laurent Souqui,*** University of Illinois at Urbana-Champaign*; Z. Zhang,* Applied Materials*; S. Liu,* University of California - Riverside*; E. Mohimi,* LAM Research*; G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign **INVITED**

Area-selective deposition of thin films affords the maskless propagation of existing substrate patterns in bottom-up fabrication of microelectronic or nanoscale devices. This can be achieved in low temperature chemical vapor deposition by identifying precursors, sometimes in combination with added inhibitors, that exhibit greatly varying nucleation delays – very short on the desired growth surface, and very long on the intended non-growth surface.Then, a growth interval can be found such that the desired film thickness is deposited on the growth surface, while few to no nuclei form on the non-growth surface.

Focusing on the deposition of metals on oxides by CVD, we investigated how selectivity for Mo, Ru, Fe and Co can be achieved between oxides of different acidity, and also between metals and oxides. We found that $Fe(CO)_5$, $Mo(CO)_6$ and $Ru_3(CO)_{12}$ afford the deposition of metal or metal carbide films on acidic oxides, but that growth is inhibited on basic oxides. On the contrary, $Co_2(CO)_8$ nucleation is faster on basic oxides than on acidic oxides. The opposite reactivity of the two carbonyl precursors towards oxide surfaces is attributed to differences in the kinetic stability of reaction intermediates on the surfaces. Additionally, the selectivity of $Co_2(CO)_8$ can be further enhanced by exposing the surface to NH_3. Finally, selectivity against metal surfaces can be achieved by first oxidizing the metal surface, then performing CVD, and finally reducing the oxide to restore the original metal surface.

11:10am **LI-ALD-WeM1-21 Inhibiting Plasma Enhanced Atomic Layer Deposition of SiO_2 on Cu using Thiol Multilayers in an ABC Cycle***, **Rohit Narayanan Kavassery Ramesh**, W. Xu, R. Gasvoda,* Colorado School of Mines, USA*; X. Lei, B. Zope, H. Chandra, R. Ridgeway, X. Jiang, G. Liu, R. Kanjolia, A. Derecskei, R. Pearlstein,* EMD Electronics, USA*; S. Agarwal,* Colorado School of Mines, USA

Atomic layer deposition (ALD) offers the potential for area-selective deposition of patterned structures to enable a bottom-up fabrication of semiconductor devices. Area-selective ALD can be achieved by selectively attaching a blocking molecule to a specific surface. SiO_2 ALD is unique in the sense that O_3 or an O_2 plasma is preferable for high throughput and cleaner process: Halogenated silane such as $SiCl_4$ and H_2O/pyridine process yield pyridinium salt as byproduct. The need for O_3 or O radicals for growth makes the use of organic blocking layers to inhibit growth challenging as hydrocarbons get rapidly combusted in the presence of O radicals. In this study, we explore area-selective, O_2-plasma-assisted ALD of SiO_2 on SiO_2 while inhibiting growth on Cu with fluorinated thiols that are resistant to combustion.

The surface species during the selective ALD on the growth (SiO_2) and nongrowth (Cu) surfaces was monitored using *in situ* reflection-absorbance infrared spectroscopy (RAIRS). SiO_2 ALD was done at 100 °C using di-sec-butyl-aminosilane (DSBAS) as the Si precursor and a remote O_2 plasma. The nongrowth surface, CMP Cu with the native oxide (CuO_x),was functionalized with 1H,1H,2H,2H-perfluorodecanethiol (Step A)at 100 °C. The *in situ* infrared spectrum of the Cu surface after functionalization showed a sharp increase in absorbance in the CF_2 stretching region (~1250 cm^{-1}) indicating thiol attachment to CuO_x. The functionalized Cu surface was then exposed to DSBAS (Step B) and O_2 plasma (Step C). The corresponding infrared spectra showed no surface O-SiH_3 species after the DSBAS cycle but indicated removal of 10-15% of the thiol after the O_2 plasma cycle. To maintain the inhibitor coverage on the surface, it was redosed in the subsequent cycle. This A-B-C type ALD process (A: PFDT, B: DSBAS, C: O_2 plasma)(see Fig. 1(a) and (b)) was repeated for 35 cycles, which yielded ~6 nm of growth on the SiO_2 surface. No evidence of SiO_2 deposition on the Cu surface was observed after 35 A-B-C cycles with RAIRS and x-ray photoelectron spectroscopy (XPS), as shown in Fig. 1 (c) and (d), respectively. Characterization of surface morphology with atomic force microscopy (AFM) revealed no evidence of damage or roughening of the Cu surface. After ALD, the inhibitor on the Cu surface was decomposed by high temperature annealing followed by cleaning of the residue with a proprietary formulation. The XPS data after cleaning indicated that Cu surface was reduced with no detectable SiO_2, as shown in Fig. 1 (e) and (f). Thus, PFDT was not only able to protect the Cu surface in an O_2 plasma process, but also inhibited the growth of SiO_2 on the Cu surface.

11:25am **LI-ALD-WeM1-24 Sequential Area Selective Deposition of Poly(3,4-ethylenedioxythiophene) (PEDOT) and Tungsten on SiO_2/Si-H Substrates***, **Hwan Oh**, J. Kim, S. Song, G. Parsons,* North Carolina State University

In nanopatterning, area-selective deposition (ASD) is gaining attention as a promising vapor-phase “bottom-up” process to overcome challenges such as edge-placement errors (EPEs) and high costs associated with the conventional “top-down” approaches.[1] However, to date, most ASD processes have addressed only individual dielectric or metal depositions. Accordingly, co-compatible integration of multiple ASD steps is desired for future advanced device fabrication. We have recently demonstrated a sequential ASD of titanium dioxide (TiO_2) and tungsten (W) films on SiO_2/Si-H line patterned substrates based on the understanding of two individual ASDs, i.e., TiO_2 ASD[2] (on SiO_2 vs. Si-H) and W ASD[3] (on Si-H vs. SiO_{-2}).

In this work, we have extended the established concept to polymeric dielectric and metal pairs, i.e., a sequential ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) and W on SiO_2/Si-H substrates (Scheme 1). In the PEDOT step, inherent PEDOT ASD on SiO_2 vs. Si-H was performed using 3,4-ethylenedioxythiophene (EDOT) as a monomer and antimony pentachloride ($SbCl_5$) as a volatile liquid oxidant *via* oxidative chemical vapor deposition (o-CVD). This process led to a thickness of ~ 13 nm PEDOT films with 10 s of o-CVD while maintaining selectivity above 0.9 (Figure 1). In the W step, W ASD on Si-H (after o-CVD) vs. PEDOT deposited on SiO_2 was conducted using sequential exposure of silane (SiH_4) and tungsten hexafluoride (WF_6) *via* atomic layer deposition (ALD). Herein, PEDOT films on SiO_2 serve as a blocking layer against W deposition, and selective deposition of W films on Si-H (after o-CVD) was confirmed by X-ray photoelectron spectroscopy (XPS) (Figure 2).

More systematic studies, for example, the origin of selectivity and film properties such as roughness and conductivity, will be investigated in the future. This concept will be demonstrated on the nm-scaled pattern substrates. Overall, we anticipate our results to offer insight into developing a more advanced process pathway to integrating multiple ASDs of polymeric low-k dielectrics and metal.

11:40am **LI-ALD-WeM1-27 Atomic Precision Advanced Manufacturing and Lessons for Area-Selective Deposition***, **Scott Schmucker**, E. Frederick, Q. Campbell, J. Ivie, E. Anderson,* Sandia National Laboratories, USA*; K. Dwyer,* University of Maryland, College Park*; A. Baczewski, G. Wang,* Sandia National Laboratories, USA*; R. Butera,* Laboratory for Physical Sciences*; S. Misra,* Sandia National Laboratories, USA

Area-selective chemisorption templated by lithographic desorption of monatomic functional groups on semiconductor surfaces has enabled a technology termed Atomic Precision Advanced Manufacturing (APAM). Among other things, APAM can be used for ultra-doping Si with n-type and p-type dopants from gaseous precursors and it is a technology extensible to other surface reactions relevant to atomic layer deposition (ALD).These gas-phase precursors are commonly hydrogenated or halogenated molecules (e.g. PH_3, AsH_3, B_2H_6, $AlCl_3$) delivered to Si(100) in ultrahigh vacuum.Within this environment, it is possible by surface characterization (e.g. scanning tunneling microscopy (STM)) and DFT modeling to understand the chemical interactions between the precursor and reactive surface sites.Additionally, electron-stimulated desorption (ESD) via STM can selectively desorb atoms from the resist at scales ranging from Angstroms to microns; thereby, dopants are precisely placed by selective chemisorption in depassivated areas in countable quantities or in two-dimensional ultra-doped films.

A distinctive advantage of APAM surface templating is the high selectivity it can realize.In the case of PH_3 on Si(100) 2×1, a hydrogen resist can provide selectivity >1000:1.One enabling factor is a link between process development and surface science.As one example, the most common defect on the Si(100) 2×1:H surface is an isolated dangling bond where a single H atom is missing. Dissociative chemisorption of PH_3 can be impeded on this defect and appropriate thermal treatment can remove reaction biproducts from the surface before dopants are incorporated into the Si lattice, preserving selectivity.

Although historically focused on dopants in semiconductors, the surface reactions of APAM are largely equivalent to ALD half-cycles.By surface functionalization and ESD, surface reactivity can be controlled for area-selective ALD. Here, we discuss efforts to generalize APAM technology to common ALD co-reactants, extend APAM beyond group-IV substrates, and assess ALD selectivity on APAM resists.

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11:55am **LI-ALD-WeM1-30 The Role of Precursor-Inhibitor Interactions in Area-Selective Atomic Layer Deposition*, Tania Sandoval,*** Universidad Técnica Federico Santa María, Chile **INVITED**

Area-selective deposition by surface deactivation has been an extensive area of research. Strategies for deactivation include the use of polymers, self-assembled monolayers, and most recently, small molecules. These inhibitor molecules act to block deposition on the non-growth area; however, the mechanisms by which selectivity is achieved and more importantly, how it is lost are still poorly understood. ASD processes are often plagued by low selectivity. Some important requirements for a good inhibitor molecule include strong adsorption and high coverage on the non-growth area, and weak (or none) interactions with the growth area, and with the incoming precursor. In the case of small inhibitor molecules, precursor-inhibitor interactions have been found to depend on the adsorption mechanism and adsorbate configurations of the inhibitor molecule, where adsorption configurations that lead to unreacted functional groups are more prone to be displaced and contribute to selectivity loss.[1]

In this presentation, theoretical studies on the fundamental understanding of the interactions between precursor and small inhibitor molecules, and the mechanism of selectivity loss will be discussed. The precursors trimethylaluminum (TMA), dimethylaluminum isopropoxide (DMAI), tris(dimethylamino)aluminum (TDMAA), and bis(diethylamino)silane (BDEAS) and inhibitor molecules acetylacetone, acetic acid, and tetramethylheptanedione were studied. The results showed that the formation of hydrogen bonds between unreacted functional groups of the inhibitor and incoming precursor lead to stronger interactions than the cases where all functional groups of the inhibitor reacted with the non-growth surface. Moreover, the results for TMA showed a higher probability to displace the inhibitor molecule than the other precursors tested, due to the more favorable interactions with the different adsorbed inhibitor configurations. Overall, this study provides fundamental insight into the importance of considering both the precursor and inhibitor molecule in achieving maximum selectivities.

[1] M.J.M. Merkx, T.E. Sandoval, D.M. Hausmann, W.M.M. Kessels, A.J.M. Mackus, Chem. Matter. 32, 3335-3345 (2020)

12:30pm **LI-ALD-WeM1-37 Spatially Controlled Atomic Layer Deposition within Polymer Templates for Multi-Material Nanorods and Nanowires Fabrication*, Rotem Azoulay,*** *T. Segal Peretz,* Technion, Israel

Today's nanofabrication techniques require multistep and costly processes in order to fabricate complex, multi-materials nanostructures. Performing atomic layer deposition (ALD) within polymeric templates can offer a simple solution for nanostructure fabrication. In this process, named sequential infiltration synthesis (SIS), high partial pressures and long exposures times lead to inorganic materials growth within polymers. Sequential polymer removal results in polymer-templated inorganic nanostructure. While SIS shows great potential in fabricating large variety of structures, it is currently limited to a single material growth process.

In this research, we demonstrated, for the first time, multi-material SIS process with control over the spatial location of each material and fabricate heterostructure nanorods and nanowires. We studied SIS within self-assembled block copolymer (BCP) films and electrospun polymer fibers and developed multi-material SIS, where two metal oxides are grown together in a single process, with precise control over their location within the polymer template. We used cylinder forming poly (styrene-block-methyl methacrylate) (PS-b-PMMA) films and electrospun PMMA as the polymeric template and DEZ (diethyl zinc), TMA (trimethyl aluminum) and $TiCl_4$ (titanium tetrachloride) as the organometallic precursors. We achieved control over the growth location of each metal oxide by tuning the organometallic precursors diffusion time, forming heterostructures after polymer removal. A short exposure of the first precursor resulted in a limited growth only at the outer part of the polymer, while a long exposure of the second precursor enabled it to reach the full depth of the polymer besides the section which was already occupied by the first precursor. An exposure to water completed the cycle. We demonstrated this process on BCP films to achieve AlOx-ZnO nanorods arrays (Figure 1) and on polymer fibers to achieve AlOx-ZnO fibers. We performed structural characterization using scanning and transmission electron microscopy (SEM and TEM, respectively) to characterize the nanowires and nanorods as well as three-dimensional characterization scanning TEM (STEM) tomography and energy-dispersive X-ray spectroscopy (EDS) STEM tomography in order to probe the structure and the chemical composition in 3D (Figure 2). This research opens new pathways for multi-materials nano scale structure fabrication through ALD-based growth within polymers.

12:45pm **LI-ALD-WeM1-40 Maskless Patterned Spatial ALD for Thin-Film Encapsulation***, C. Frijters,* SALDtech B.V., Netherlands*; Y. Creyghton,* Holst Centre / TNO, Netherlands*; **Paul Poodt,*** SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD is flat panel (OLED) displays. Examples include semiconductor and dielectric layers for use in thin-film transistors, and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

Encapsulation of OLED devices requires thin, dense films with very low pinhole densities and water vapor transmission rates. In most cases, the materials used are dielectric (e.g.SiN and Al2O3) and deposition of these materials on electrical interconnects placed next to the OLED device is undesirable. In case PECVD or PVD is used to deposit encapsulation layers, shadow masks can be used to prevent deposition on the interconnects. However, shadow masks will not work in combination of ALD as there will be substantial deposition under the mask as ALD is a high step coverage method.

We are developing a mask-less, plasma enhanced Spatial ALD method to do direct patterned deposition, only on the devices and prevent deposition in between. It uses a similar approach to patterned deposition as used in slot-die coating, by combining intermittent coating with stripe coating to deposit rectangular patterns of tunable dimensions. Essential is the use of an atmospheric pressure plasma source that can be switched on and off efficiently to pattern the deposition. The main challenge is to achieve sharp transitions between film and no film, where the target is to reach a transition width of approximately 200 µm, similar to the transition width achieved in e.g. PECVD in combination with shadow masks.

We will explain how we do mask-less patterned deposition and how the transition width can be minimized through a combination of optimizing both the ALD process as well as the spatial ALD injector design. Finally we will show results of mask-less patterned deposition by Spatial ALD on substrate sizes as large as 30 cm x 40 cm and explain how we will scale up to substrate sizes of 1.5 m^2 and beyond.

1:00pm **LI-ALD-WeM1-43 Y_2O_3 Atomic Layer Deposition Process Scale-Up to Very Large Batch Size*, Lassi Leppilahti,*** *P. Päivike, M. Saarniheimo, S. Sneck,* Beneq, Finland

Yttrium oxide (Y_2O_3) thin film coatings have shown great potential as fluoride plasma resistant protective coatings on semiconductor process equipment parts. Many of these parts are large with complex designs often containing high-aspect-ratio gas channels making them challenging to coat. Conformal, dense and pinhole free ALD coatings overcome these challenges and enable more stable processes, greater yields, and longer service times between maintenance. Here we report the results from a study on the very large batch scalability of ALD yttrium oxide. 30 mock-up showerhead parts were coated in a Beneq P800 reactor at 250 °C using tris(methylcyclopentadienyl)yttrium ($(MeCp)_3Y$) and water (H_2O) as the precursors. The reaction chamber was loaded with the mock-up showerhead parts slotted in 15 stacked frames. The total surface area of the reaction chamber inner surfaces, frames and substrates was 22.1 m^2 without considering the surface roughness. The film quality was evaluated on silicon pieces cut from blank wafers spread throughout the reaction chamber. Preliminary ellipsometry results showed ±8 % 1σ within-batch non-uniformity. The growth-per-cycle ranged between 2.13 Å/c and 2.54 Å/c. The high growth per cycle is believed to be caused by the strong water adsorption on the yttrium oxide surface resulting in a CVD-like component in the deposition process. A handful of characterisation techniques were used to determine the film composition. ToF–ERDA showed the film was close to stoichiometric Y_2O_3. LA–ICP–MS analysis revealed the film contained little impurities. XRD confirmed the microstructure was cubic yttria. This contribution describes the process scale-up in more detail, discusses the related challenges and summarises the latest results.

1:15pm **LI-ALD-WeM1-46 Low Temperature Thermal Atomic Layer Deposition of Elemental Tellurium Using and a Novel Tellurium Precursor and Nitrogen-Based Coreactants***, A. Upadhyay,* Wayne State University*; K. Woods,* Applied Materials*; M. Saly, T. Knisley,* Applied Materials Inc.*;* ***Charles Winter,*** Wayne State University

Phase change memory (PCM) is made possible by the large difference in resistivity between the amorphous and crystalline forms of certain materials. Heating either form by light pulses or electrically leads to cycling between the amorphous and crystalline states. The most widely studied PCM is $Ge_2Sb_2Te_5$ (GST), because of its non-volatility, scalability, fast conversion between amorphous and crystalline states, and extremely long service life. There is considerable interest in the atomic layer deposition (ALD) growth of GST, because of the thickness control and conformal coverage and also because some properties of GST are improved in thinner films (rate of amorphous to crystalline state interconversion). Previous ALD growth chemistry has relied largely upon silyl elimination reactions between halides or alkoxides and Sb and Te trialkylsilyl compounds. While these ALD routes have provided desired thin films, they target specific stoichiometric compositions such as GeTe, GeSb, Sb_2Te, Sb_2Te_3, and others. There is recent interest in controlling the element compositions in GST beyond the $Ge_2Sb_2Te_5$ composition, to adjust properties such as crystallization temperatures and resistivities. Moreover, many of the currently available Ge, Sb, and Te ALD precursors have low thermal stabilities, which limit their upper deposition limits often to temperatures below 100 °C. This issue is most acute with Te precursors, since the electrochemical potential of Te ion is most positive among the three element ions ($E° Te^{4+} \leftrightarrow Te = 0.568$ V; $E° Ge^{2+} \leftrightarrow Ge = 0.24$ V; $E° Sb_2O_3 + 6 H^+ + 6 e^- \leftrightarrow 2 Sb + 3 H_2O = 0.152$ V). Herein, we will describe the ALD of elemental tellurium (Te) films using novel tellurium precursors and nitrogen sources such as hydrazine. These precursors presumably form Te_3N_4, which is unstable and loses N_2 to afford elemental Te. Properties of these tellurium precursors will be described. A liquid Te precursor with a decomposition temperature of 257 °C was identified from this screening. ALD studies revealed growth temperatures between 75 and 200 °C, although highly crystalline, rough films were obtained at >110 °C. The growth rate was 0.10 Å/cycle at substrate temperatures of 75 to 100 °C. X-ray diffraction showed elemental Te in the hexagonal phase. The composition of the film was evaluated using X-ray photoelectron spectroscopy and showed high purity Te.

1:30pm **LI-ALD-WeM1-49 When Complex Becomes Complicated – Strategies for Succeeding with Arduous Ternary Oxide Processes***,* ***Henrik Soensteby,*** University of Oslo, Norway **INVITED**

Atomic layer deposition (ALD) has been an invaluable technique in the miniturization of electronic components over the last 15 years. As continued downscaling is pushing silicon technology to its inherent physical limits, the community is looking for new materials, technologies and architectures to inherit the Si-hegemony. With ALD being a mature deposition technique in electronics industry, it is in a unique position to take part in new paradigms within microelectronics. A requirement is that ALD can provide processes for new functional and technologically relevant materials under conditions that are attainable to the microelectronics industry.

Complex oxides come in a wide variety of flavours. High-k dielectricity, ferroelectricity, memristivity and metallicity are believed to be important properties in future electronics and can all be found in different complex oxides, *e.g.* $SrTiO_3$, $BaTiO_3$, $SmNiO_3$ and $LaNiO_3$, respectively. Unfortunately, deposition of high quality films of complex oxides, with a few exceptions, have been limited to physical techniques such as pulsed laser deposition and molecular beam epitaxy.

With recent progress in ALD of complex oxides, however, the ALD toolbox of functional materials is growing fast. Concurrently, this has lead to increased understanding in the growth- and control mechanisms of ternary+ oxides. This includes effects of precursors, temperature, sub-cycle arrangements, co-reactants, substrates *etc.*

In this talk, I will discuss how and why a range of variables affect complex oxide ALD. I will convey some strategies that have allowed us to develop a broad range of complex oxide processes, and try to generalize in a set of tips and tricks for complex process development. Complex does not have to be complicated, but thoughtful process development is a requirement to succeed!

1:50pm **LI-ALD-WeM1-53 Announcement of ALD and ALE Student Awardees, Closing Remarks & Thank Yous***,* ***Scott Clendenning,*** Intel

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

Live Session
Room Live - Session LI-ALD-WeM2

AM/AF (in-situ metro) Live Session

Moderators: Dr. Alex Martinson, Argonne National Laboratory, Dr. Nathanaelle Schneider, CNRS-IPVF, Dr. Virginia Wheeler, U.S. Naval Research Laboratory

9:30am **LI-ALD-WeM2-1 Welcome, Thank Yous & Instructions***, **Nathanaelle Schneider,*** CNRS-IPVF, France

Thank you for attending today's session! We hope you will enjoy the session!

9:35am **LI-ALD-WeM2-2 Surface Modification of TiO_2 Nanoparticles by Ultrathin SiO_2 Films, Cu_2O and Pt Nanoclusters for Enhanced Photocatalytic Activity Using Atomic Layer Deposition in a Fluidized Bed Reactor: A Comparative Study***, **Hao Van Bui,*** Phenikaa University, Viet Nam*; D. Benz, J. van Ommen,* Delft University of Technology, Netherlands **INVITED**

Titanium dioxide (TiO_2) is the most popularly used photocatalyst in many practical applications, such as air purification, water treatment, and hydrogen production due to its excellent photocatalytic properties, high structural and chemical stabilities, low environmental impact, and abundance in nature. However, the rapid recombination of photogenerated electrons and holes is a major limiting factor to achieve high photocatalytic efficiencies. To address this issue, the surface of TiO_2 is usually engineered by coupling with a thin film or nanoclusters of other materials. This is to promote the charge transfer at the interface between the TiO_2 and the deposited materials, which consequently reduces the charge recombination in the TiO_2.

Due to their high catalytic activities, noble metals are most popularly used. In addition to promoting electron transfer, noble metals can also act as co-catalysts, providing further catalytic enhancement. Nevertheless, long exposures to UV-irradiation may cause local photocatalytic oxidation of the metal at the metal/TiO_2 interfaces, which creates new electron-hole recombination centers and consequently decreases the photocatalytic efficiency. In addition, despite their excellent activity, the use of noble metals is not desirable due to their high cost and scarcity, especially for large-scale production. Therefore, the surface modification of TiO_2 by oxides such as CuO, Cu_2O, Fe_2O_3, and SiO_2 has recently been more attractive.

Our presentation will focus on the use of ALD in a fluidized bed reactor operating at atmospheric pressure (APALD-FBR) for the surface modification of TiO_2 nanoparticles. Three different ALD processes are demonstrated: ALD of ultrathin SiO_2 films using $TiCl_4$ and H_2O, ALD of Cu_2O using Cu(I)(hfac)(TMVS) and H_2O, and ALD of Pt using $MeCpPtMe_3$ and O_2. We will show that APALD-FBR not only provides the ability to control the deposition of SiO_2, Cu_2O, and Pt at the sub-nanometer scale but also enables the deposition at temperatures significantly lower than the conventional ALD processes. We will further demonstrate that the photocatalytic activity of TiO_2 depends strongly on the loading of the deposited material (SiO_2, Cu_2O, or Pt) and by controlling the loading, the photocatalytic activity of TiO_2 can be significantly enhanced. A comparison of the photocatalytic activities of TiO_2/SiO_2, TiO_2/Cu_2O, and TiO_2/Pt photocatalysts toward the degradation of various organic dyes will be presented and discussed.

9:55am **LI-ALD-WeM2-6 In-Situ High Temperature XRD of Atomic Layer Deposited Gallia-Ceria Mixed Oxides***, **Fatemeh Gashoul Daresibi,*** University of Tehran, Iran*; M. Heikkilä, M. Ritala,* University of Helsinki, Finland*; A. Khodadadi, Y. Mortazavi,* University of Tehran, Iran

Ceria is well-known for its oxygen storage-release capacity [1]. Catalytic behavior of ceria can be tuned by mixing it with different oxides including those of V [2], Ga [3] and Zr [4]. Although the control on the stoichiometry and close contact of oxides is highly challenging [5], recent studies on atomic layer deposition [6] showed its capability in synthesizing conformal and uniform film with atomically precise control of composition.

Herein, we synthesized $Ga_xCe_yO_z$ with super-cyclic ALD using $Ce(thd)_4$, $Ga(acac)_3$ and O_3. Studies on the growth rate showed surface enhanced and linear growth at low and high number of cycles respectively. The in-situ HT-XRD of pure ceria showed changes of crystal structure at high temperatures starting from 650°C under H_2 and a constant lattice structure under air. The XRD pattern of $Ga_xCe_yO_z$ in oxidizing atmosphere under air did not show any specific peak from RT up to 600°C due to incorporation of Ga in cerium oxide and then characteristic peaks of crystalline ceria appeared at higher temperatures as a sign of segregation and phase separation [7]. In reducing atmosphere, under H_2, the evolution of a weak crystalline structure was monitored which peered to be related to the ceria when the partially reduced gallium oxide started to evaporate and leave the mixed oxide film [8]. The results showed that this surface segregation only happens at temperatures high enough to locally reduce and sublime the gallium species. Ex-situ Raman spectra and atomic force microscopy of the samples calcined at various temperatures also confirmed the crystallization/roughening of the films at high calcination temperatures. Therefore, the ALD-$GaCeO_x$ thin film keeps its amorphous mixed structure stable up to around 600°C suitable for many catalytic reactions.

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10:10am **LI-ALD-WeM2-9 Using Ambient Pressure X-Ray Photoelectron Spectroscopy to Study ALD in real-time***, **Esko Kokkonen,*** Max IV Laboratory, Sweden*; M. Kaipio, H. Nieminen,* University of Helsinki, Finland*; F. Rehman,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; M. Putkonen, M. Ritala, S. Huotari,* University of Helsinki, Finland*; J. Schnadt,* Lund University, Sweden*; S. Urpelainen,* University of Oulu, Finland

Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful tool to study surfaces in elevated pressure and temperature conditions. We have recently developed an ambient pressure cell (AP cell) dedicated to ALD research. The cell allows studying the surface of a substrate where ALD reactions take place. Importantly, since the cell makes it possible to conduct XPS measurements at millibar pressure regimes, it is possible to measure the chemical state of the surface in real-time as the ALD precursors react with the surface. The cell is intended for chemical characterization of intermediate products that are short-lived and might not be present on the surface once saturation of the surface has been achieved and therefore are not visible in post-process XPS identification. Experiments such as these have gained noticeable traction within a few years. [1,2]

The system is installed on the SPECIES beamline [3] at the MAX IV Laboratory in Lund, Sweden. SPECIES is a soft X-ray beamline with one beam branch dedicated to APXPS. The beamline offers a wide photon energy range of 30-1500 eV, which enables to study most core-levels using XPS, but also makes it possible to focus on valence band investigations using UPS and lower photon energies and high photon flux. The endstation consists of different equipment for sample characterization and preparation, with the main instrument being an electron analyser capable of high energy and time resolution.

The ALD cell has been designed with realistic gas flow dynamics in mind. The cell can be operated with a maximum pressure of 20 mbar, with the intention of creating a laminar-like flow across the substrate surface that is being investigated using XPS. The outlet (pump) line of the cell is connected to a quadrupole mass spectrometer (QMS) via a leak valve. The QMS allows to simultaneously follow masses of important ligands and synchronize this data acquisition with the XPS data.

Here, we will give a brief overview of the system including its design and operating parameters. Some results from example cases are given which demonstrate the capability of the ALD cell for studying substrates during ALD reactions.

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10:25am **LI-ALD-WeM2-12 Observing the Crystallization of Ultrathin Alumina and Polymorphic Transformations of Gallium Oxide Using *in Situ* Reflection High Energy Electron Diffraction***, **Alexandra Howzen**, N. Strandwitz,* Lehigh University

The maximum amount of thermal energy available during atomic layer deposition (ALD) is generally determined by the decomposition temperature of the precursors which also sets the maximum temperature for the "ALD window". This maximum temperature limits the structural perfection and extent of crystallization in resulting films for many ALD precursor chemistries. Intermittent annealing during the film growth in between ALD chemical exposures has been explored previously and is shown to increase the density and quality of ALD films[1]. However, the ability to directly monitor structural changes of ALD films is expected to provide new insight regarding film crystallization temperature, surface roughening, and dependence on gas ambient.

In this work, we integrate reflection high energy electron diffraction (RHEED) into a home-built ALD system to monitor structural and morphological transformations during ALD growth and thermally-induced structural transformations. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. We will use *in situ* RHEED to observe the thermal crystallization of an ultrathin, amorphous alumina film deposited on sapphire. Similarly, we will show the thermally induced structural evolution of an ultrathin (1-20 ALD cycles) Ga_2O_3 film deposited on sapphire with TMGa/O_2 precursors. Ga_2O_3 films display multiple polymorphs (α, β, γ, δ, ε) which can be controlled depending on substrate crystal structure and crystallization temperature. Therefore, this work shows the structural transformations available to ultrathin Ga_2O_3 films deposited by ALD as a function of temperature up to the film's complete desorption. The integration of RHEED with ALD offers a slow-motion picture of the structural transformations that occur during traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

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10:50am **LI-ALD-WeM2-17 Novel Functional Metal-Organic Materials by ALD/MLD***, **Maarit Karppinen,*** Aalto University, Finland **INVITED**

Atomic layer deposition (ALD) technology is one of the cornerstones of modern microelectronics, where it is exploited in the fabrication of high-quality conformal inorganic thin films. Its counterpart for organic thin films – molecular layer deposition (MLD) – has also been known for long but little exploited. Currently, the hybrid of these techniques – ALD/MLD – is strongly emerging as a state-of-the-art route for designer's metal-organic thin films. In ALD/MLD, a metal-bearing precursor is combined with an organic precursor to deposit metal-organic thin films in which the organic molecules naturally link the metal atoms. Interestingly, some of these processes yield in-situ crystalline films. Another intriguing aspect is that many of the metal-organic materials realized through ALD/MLD are fundamentally new and difficult if not impossible to be obtained through conventional synthesis. In this presentation my intension is to [1-7]: (*i*) briefly introduce the breath of the ALD/MLD processes developed, (*ii*) address the constraints/possibilities for growing in-situ crystalline metal-organic thin films, and (*iii*) highlight some exciting ALD/MLD materials and their application potential e.g. in microbatteries, solar cells and flexible magnets.

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11:10am **LI-ALD-WeM2-21 Ultrathin Hybrid Siloxane-Alumina Dielectric Films by Ring Opening Molecular Layer Deposition of Cyclic Tetrasiloxane***, **Kristina Ashurbekova,*** Dagestan State University , Russian Federation*; K. Ashurbekova,* CIC nanoGUNE BRTA, Spain*; I. Saric,* University of Rijeka , Croatia*; M. Gobbi, E. Modin, A. Chuvilin,* CIC nanoGUNE BRTA, Spain*; M. Petravic,* University of Rijeka, Croatia*; I. Abdulagatov,* Dagestan State University, Russian Federation*; M. Knez,* CIC nanoGUNE BRTA, Spain

Siloxane-based materials have gained interest for various important applications such as insulating layers in microelectronics, thin film encapsulation layers, biocompatible coatings, and barriers. The ring-opening polymerization (ROP) of cyclic siloxanes is a way to synthesize such materials using solution-based techniques and is a rare example of an entropically driven polymerization. The vibrational and rotational freedom achievable in the linear siloxane units is much greater than in the cyclic structures. In this work, we introduce cyclic siloxanes as a new class of silicon precursors for ROP- Molecular layer deposition (MLD), uncommon because of the lack of reactive groups, but reactive because of the ring structure of the cyclosiloxane.

MLD is a powerful vapor phase approach for growing thin polymer films with molecular level thickness control. In the present work, hybrid organic-inorganic siloxane-alumina films were grown by applying a ring-opening MLD using sequential surface reactions between 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4) and trimethylaluminum (TMA). *In-situ* QCM analysis showed a linear mass increase with the number of MLD cycles within a processing temperature window between 120 and 200 °C and revealed a self-limiting surface chemistry between TMA and V_4D_4. A growth per cycle of 1.4 and 1.6 Å and a density of 1.9 and 2.2 g/cm^3 were determined by X-ray reflectivity (XRR) for the V_4D_4/TMA film deposited at 150 and 200 °C, respectively. X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and in-situ QCM were employed to analyze the structural changes, composition of the film and to suggest a realistic V_4D_4/TMA reaction mechanism. High-resolution transmission electron microscopy (HRTEM) showed that the MLD process enables the formation of highly conformal coating of zirconia nanoparticles. The grown siloxane-alumina film, even as thin as 12 nm, showed an extremely low leakage current density (lower than 5.1×10^{-8} A cm^{-2} at ± 2.5 MV cm^{-1}), a dielectric constant (k) of 4.7, and a good thermal stability after one-hour annealing in air at 1100 °C. The pinhole-free nature and conformal growth inherent to the MLD technique allow the formation of high-quality siloxane-alumina thin films withexcellent insulating properties and thermal stability that are promising as ultrathin insulating coatings in field-effect transistors, flash memories, and capacitors in modern electronic systems. [1]

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11:25am **LI-ALD-WeM2-24 Optically Controlled Large-Coercivity Room-Temperature Thin-Film Magnets Through ALD/MLD***, **Anish Philip**, M. Karppinen,* Aalto University, Finland

Optically controlled magnetic materials could enable magnetic ultra-fast recording at high density. Such dream materials designed from multiple functionalities could open new horizons for many other application fields as well requiring photo-controlled nanoswitchers.[1] Though there are several families of photomagnetic materials known, including the prussian blue analogues,magnetic nanoparticles modified with photochromic molecules and inorganic materials intercalated with photoresponsive molecules, the real challenges of discovering photo-magnets performing at room-temperature and fabricated in thin films using an industrially feasible technology have never been addressed.

Here we address the challenge by taking the advantage of the atomic/molecular layer deposition (ALD/MLD) technique.[2–4]We deposited ε-Fe_2O_3:azobenzoate superlattice structures with sub-nm scale accuracy from $FeCl_3$, H_2O and azobenzene-4,4′-dicarboxylic acid precursors. The ε-Fe_2O_3 phase was chosen due to its unique room-temperature multiferroic properties including an exceptionally high coercive field.Azobenzene is a well-known photochromic molecule and has been used for integrating into several functional materials as it undergoes reversible isomerization (trans-cis) around the N=N bond upon light irradiation of suitable wavelengths.By combining the RT hard ferrimagnet ε-Fe_2O_3 and the photoresponsive azobenzene,we demonstrate the reversible photo-switching functionality on the coercivity and magnetization values with alternating irradiations of the films with UV and visible light. Interestingly, the azobenzene layers not only add the switching functionality but also enhance the overall magnetic performance of the ε-Fe_2O_3 matrix. For example, the room-temperature coercivity was found to be 2.6 kOe for ε-Fe_2O_3-azobenzoate superlattice structures, while it was 2.0 kOe for a ε-Fe_2O_3 film of the same overall thickness.

A vibrating sample magnetometer (VSM) was used for studying the magnetic properties of the films. The structure, chemical composition and photoresponsive nature of the films were investigated using XRR, GIXRD, SEM, FTIR and UV-Vis studies.

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11:40am **LI-ALD-WeM2-27 Deposition of Thermally Stable Polybenzimidazole (PBI) Thin Films by Molecular Layer Deposition Technique***, **Saba Ghafourisaleh**, M. Leskelä, M. Putkonen, M. Ritala,* University of Helsinki, Finland

We report the deposition of polybenzimidazoles (PBI) thin films with Molecular Layer Deposition (MLD) for the first time. Imidazole derivatives are known to be thermally stable and withstand harsh acidic, basic, and oxidizing environments. MLD process for PBI-like polymers would open up numerous application fields where conformal organic thin films can be used as protective layers for more sensitive materials, like thermally resistant textile fibers, thermal insulation parts of semiconductor devices, high-temperature matrix resins, adhesives, and foams. Previously inorganic ALD materials, like Al_2O_3, have been used for protecting polymers.[1,2]

Isophthalic acid (IPA), 3, 3'-diaminobenzidine (DAB) were used as monomers and TMA was used as a promoting precursor in this process. The monomers were pulsed and purged sequentially and the condensation reactions of the adsorbed monomers on the surface resulted in PBI thin film growth with growth are of 6.0 Å/cycle. PBI films were characterized in detail by FTIR, SEM, TGA/DTA, and AFM.

Sublimation temperatures for the IPA and DAB were 160-165 ^oC and 210-220 ^oC, respectively. The reaction temperature was within a range of 225-300 ^oC. The films were uniform and transparent on a silicon substrate. The thickness non-uniformity along the 5x5 cm^2 substrate was less than 2 %. The films were smooth with a low degree of roughness (500 nm x 500 nm, Rq=0,48 nm for 1µm thick film). Thermogravimetry (TGA) analysis in nitrogen (N_2) and air showed that PBI films were thermally stable.

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11:55am **LI-ALD-WeM2-30 Future of Membrane Separations through Atomic Layer Processing***, **David Bergsman**,* University of Washington **INVITED**

Recent years have seen a surge of interest into improving the scalability of atomic layer processing (ALP) tools, such as work in spatial atomic layer deposition (ALD), molecular layer deposition (MLD), and vapor-phase infiltration (VPI). This improved scalability, along with a continued decrease in the cost of these processes, has allowed these tools to be considered outside the semiconductor industry, such as in solar cells and battery electrodes. These are technologies for which precise control over thickness, structure, and composition is critical to achieve optimum device performance. One technology area that has yet to see commercialization of these tools is in membrane separations. Similar to solar cells and batteries, membranes also rely upon precise materials properties to operate effectively, requiring narrow pore size distributions, non-fouling surface chemistries, and robust rheological properties. As a result, membranes are an excellent candidate for the implementation of atomic layer processing tools in their synthesis.

This presentation will highlight the potential use of atomic layer processing tools for membrane separations, reviewing recent advancements in this area. Generally, these tools can either be used to enhance an already existing material, such as by coating a porous structure or infiltrating a bulk material, or they can be used to create the selective layer itself, through the deposition of a thin selective layer. First, the use of ALD, MLD, and VPI to enhance membrane performance will be highlighted, including work to decorate membrane surfaces, control pore sizes, and infiltrate polymers to impart conductivity or chemical resilience. Then, cases where ALD and MLD have been used to create the active separating layer will be discussed, such as in ALD-based inorganic ion conductors, MLD-based desalination membranes, and hybrid ALD/MLD-based porous layers. Finally, promising future directions and the improvements that will ultimately be necessary for these tools to be used in commercial membrane synthesis will be explored.

12:30pm **LI-ALD-WeM2-37 Molecular Layer Deposition of All-Organic Polyamide Nylon 6,2***, **Marcel Junige**, S. George,* University of Colorado at Boulder

We developed an MLD process for the all-organic polyamide nylon 6,2 using separate, sequential exposures of ethylene diamine and adipoyl chloride. Our hot-wall, viscous-flow vacuum reactor featured a small gas volume, laminar gas flow conditions, and isothermal heating. We utilized *in situ* spectroscopic ellipsometry (iSE) to study MLD nucleation and growth; as well as x-ray reflectometry (XRR), atomic force microscopy (AFM), x-ray photoelectron spectroscopy, Raman spectroscopy, and grazing-incidence small- & wide-angle x-ray scattering to characterize MLD film properties.

In the steady-state growth regime, iSE verified the MLD characteristics: Multiple exposures of neither monomer alone could produce a significant thickness gain; both the half-reactions were self-terminating. The MLD exhibited a linear growth per cycle (GPC) of 3.7 Å at 115ºC. The GPC decreased by approximately 1/3 with every 10ºC increase in temperature.

The refractive index of a ~100 nm nylon 6,2 MLD film was extracted from an iSE multi-time-slice analysis and exhibited uniaxial anisotropy. This anisotropy indicated an orderly alignment of individual polymer chains. Amine hydrogen from one polyamide chain can bridge bond with carbonyl oxygen from another. These intermolecular forces can hold nylon chains together very tightly. XRR measured a mass density of 1.38 $^{g}/_{cm^3}$, matching the calculated crystal density value. AFM imaged the surface of a ~17 nm nylon 6,2 MLD film: The rms roughness of 4.4 Å was characterized from the topography image; the Young's modulus, averaging 3.6±0.5 GPa, was extracted from force-distance curves in pinpoint mode at every pixel. This verified uniform nanomechanical film properties without pinholes.

We also tested the stability of nylon 6,2 MLD films in various atmospheres at temperatures from 115 to 350ºC. Nylon 6,2 MLD films started to lose thickness in argon around 150ºC. Neither acetone vapor nor molecular oxygen etched nylon 6,2 at 135°C. In contrast, hydrogen peroxide vapor and ozone spontaneously etched nylon 6,2.

In related work, we have demonstrated area selectivity of nylon 6,2 MLD on industrial test features with nucleation and growth on amorphous carbon lines versus inhibition on passivated silica trenches.[1] We utilized secondary electron microscopy to image the test features before and after area-selective MLD. This demonstrated the potential to repair the amorphous carbon hard mask that eroded by reactive ion etching during pattern transfer. The all-organic polymer nylon 6,2 was preferable because no residue was left after ashing of the MLD films.

17. *JVST A* **39**, 023204 (2021).

12:45pm **LI-ALD-WeM2-40 Vapor Phase Conversion of Pt Nanoparticles Into Pt-Sn Bimetallic Nanoparticles*, Nithin Poonkottil,*** *R. Ramachandran,* Ghent University, Belgium*; E. Solano,* ALBA Synchrotron, Spain*; N. Veeraraghavan Srinath, J. Feng, A. Werbrouck, M. Van Daele, M. M. Minjauw, M. Filez, H. Poelman,* Ghent University, Belgium*; A. Coati,* Synchrotron SOLEIL, France*; C. Detavernier, J. Dendooven,* Ghent University, Belgium

Bimetallic nanoparticles (BMNPs) offer interesting size and composition-dependent properties. Pt-Sn BMNPs are important in the field of catalysis, highlighted by their widespread industrial use for propylene production. They are widely accepted as a model system in fundamental studies of structure-performance relationships. ALD has proven successful in preparing catalytic systems with fine control over NP sizes and compositions, but the creation of non-noble metal-containing alloys often requires a high temperature reduction step. We report the vapour phase conversion of Pt NPs into Pt-Sn BMNPs based on the selective decomposition of tetrakis(dimethylamido)tin (TDMASn), a common Sn ALD precursor, on Pt, which induces a solid-state reaction of metallic Sn with Pt to form BMNPs at low temperature.

The decomposition of ALD precursors is often mainly considered a temperature dependent property. However, TDMASn provides an example where the precursor decomposition is also a substrate dependent property. We found that TDMASn selectively decomposes on Pt in a temperature range of 150-300°C, whereas no decomposition was observed on other substrates like SiO_2, Al_2O_3 and TiN (Fig.1a). The decomposition of TDMASn on Pt thin films led to the formation of different Pt-Sn alloys (Fig.1b). The exposure of ALD-grown Pt NPs (Fig.2a) to TDMASn pulses resulted in their conversion to Pt-Sn BMNPs, but the conversion process induced extensive particle ripening, leading to large and non-uniform particle sizes, undesired for catalytic applications (Fig.2c). Interestingly, the conversion process could be improved by using an alternating pulsing sequence of TDMASn and H_2 exposures. The introduction of H_2 substantially aids in retaining the small NP sizes of the original Pt NPs (Fig.2b). In situ mass spectrometry data during this process showed the removal of organic ligands during the H_2 pulse. The Sn uptake was monitored by in situ X-ray fluorescence (XRF), revealing saturation of the Sn incorporation in the Pt NPs as a function of the number of TDMASn-H_2 conversion cycles (Fig.3a). Moreover, the amount of inserted Sn can be controlled via the deposition temperature. PtSn versus Pt_3Sn is accomplished by varying the deposition temperature during this process from 150-250°C (Fig.3b). Finally, we confirmed the compatibility of this method with high surface area supports by the successful conversion of a mesoporous Pt/SiO_2 catalyst.

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This work is funded by the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No.765378.

1:00pm **LI-ALD-WeM2-43 Atomic Layer Deposition of Zirconium Sulfide*, Xiangbo Meng,*** University of Arkansas

Zirconium disulfide (ZrS_2) is one of two-dimensional (2D) transition metal dichalcogenides (TMDs), which is promising in many applications, such as lubrication, optoelectronic, catalysis, and energy storage. However, few studies have been devoted to developing ZrS_2. As a unique technique, atomic layer deposition (ALD) has been reported for a variety of sulfide processes in the past decades and recently emerged as a new tool for nanofabrication of 2D TMDs.[1, 2] Using tetrakis(dimethylamido)zirconium(TDMA-Zr) and 4% H_2S as precursors, recently we have developed a novel ALD process to grow ZrS_x. Similar precursors have been used in our previous studies.[3-5] We first investigated the ALD ZrS_x process using an *in situ* quartz crystal microbalance (QCM) and our QCM measurements confirmed repeatable saturation growth of ZrS_x at different temperatures. Our study further revealed that this ALD process enables large-scale growth of nanoscale ZrS_x films uniformly in the temperature range of 75 – 300 ℃ on various substrates. Furthermore, we characterized the ALD ZrS_x films using a suite of tools, including scanning electron microscopy, transmission electron microscopy, synchrotron-based X-ray diffraction, and X-ray photoelectron spectroscopy to clarify their morphology, crystallinity, and composition. We found that the growth of ZrS_x per cycle decreases from 1.17 Å/cycle at 75 ℃ to 0.28 Å/cycle at 300 ℃. In addition, our work revealed that the crystallinity and composition of ZrS_x compounds vary with deposition temperature. This study may pave an avenue to grow large-scale 2D ZrS_2 films, which potentially provide new solutions to some emerging applications.

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1:15pm **LI-ALD-WeM2-46 Vapor Phase Infiltration of Titanium Tetrachloride Into Polyaniline (PANI): Process Kinetics, Electronic Properties and Optical Response*, Mark Losego*,** *S. Gregory, Y. Li, K. Malinowski,* Georgia Tech

This talk with discuss our use of vapor phase infiltration (VPI) to alter the optoelectronic properties of conducting polymer poly(aniline) (PAni). VPI is similar to atomic layer deposition (ALD), but instead of cycling viscous flows of co-reactants, VPI doses a single reactant vapor in a static atmosphere followed by a pump-purge cycle. ALD typically provides conformal surface coatings while VPI enables extensive sub-surface diffusion and reactions within organic substrates. In particular to our study, PAni was VPI treated with a single cycle of $TiCl_{4--}$-H_2O, and the resulting hybrid films showed unique optoelectronic properties that have not been previously reported. As VPI hold time increased, PAni films turned from blue to nearly transparent to green. This color transition is because of the formation of polaronic charge carriers concomitant with the formation of TiO_x; the polaronic carriers absorb the red-NIR-MIR spectra (700- 5000 nm) while TiO_{-x} absorb the blue-UV region (450 - 350 nm). This combination of optical absorbances in PAni has not been observed before. Furthermore, these polaronic carriers enabled electrical conductivities as high at 0.2 S/cm. By varying the $TiCl_4$ exposure time and measuring *ex-situ-* optical signatures, an effective diffusion coefficient of *ca.* $1\cdot10^{-15}$ cm^2/s was measured. Lastly, XPS measurements elucidated a reaction mechanism for the formation of TiO_{-x} and PAni polarons. Both oxidative doping and acid doping due to the HCl byproduct is observed. By better understanding this reaction mechanism and kinetics, ALD and VPI can be optimized for future organic semiconductor doping processes.

1:30pm **LI-ALD-WeM2-49 Atomic/Molecular Layer Deposition for Batteries Materials*, Chunmei Ban,*** University of Colorado Boulder **INVITED**

The atomic layer deposition (ALD) technique has proven itself to be the best method to deposit continuous, conformal and pinhole-free films. Ultrathin metal oxides coating via ALD has been applied on battery materials in mitigating the parasitic side reactions between the electrolyte and the electrode surface, which results in the greatly improved performance of lithium-ion electrodes. Based on the similar deposition mechanism, we have developed molecular layer deposition (MLD) to integrate organic groups into the metal oxides matrix, in order to simultaneously address both mechanical strength and surface stability. It is found that the inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and gradual electrolyte consumption during operation. Such interaction between electrolyte and electrode becomes more pronounced for intermetallic alloy and lithium-metal anode materials and high-voltage cathode materials. This presentation will discuss the mitigation strategies which are based on atomic/molecular deposition techniques and their impact on electrochemical behavior of battery materials. With the capability to modify the surface and interface through the control of composition, thickness and mechanical properties, MLD would chemically or physically change the surface chemistry and structure of battery materials, while accommodating dramatic volumetric change associated with high-capacity intermetallic anodes. Combining with the results from advanced characterization techniques, this talk will emphasize the unique chemical interaction between the electrolyte and the surface of intermetallic electrodes, and exploit surface modification strategies to dictate the interface chemistry and manipulating the chemi-physical properties of the electrode-electrolyte interphase for efficient electrochemical reactions.

1:50pm **LI-ALD-WeM2-53 Announcement of ALD and ALE Student Awardees, Closing Remarks & Thank Yous*, Seán Barry,*** Carleton University, Canada

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

Live Session
Room Live - Session LI-ALE-WeM3
Atomic Layer Etching Live Session II

Moderators: Prof. Satoshi Hamaguchi, Osaka University, Japan, Dr. Angelique Raley, TEL Technology Center, America, LLC, USA

9:30am **LI-ALE-WeM3-1 Welcome, Thank Yous, & Instructions***, **Satoshi Hamaguchi**,* Osaka University, Japan*; A. Raley,* TEL Technology Center, America, LLC

Thank you for attending and we hope you will enjoy the session!

9:35am **LI-ALE-WeM3-2 Precise Atomic Layer Control of 2D MoS_2 by ALE Technique for Device Applications***, **Geun Young Yeom**,* Sungkyunkwan University, Republic of Korea*; K. Kim, J. Kang,* Sungkyunkwan University, Korea, Korea (Democratic People's Republic of)*; K. Kim,* Sungkyunkwan University, Korea, Massachusetts Institute of Technology **INVITED**

One of the two dimensional chalcogenide materials, MoS_2, is widely investigated as potential next generation devices for photodetector, solar cell, biomedical devices, etc. especially due to the change of bandgap energy and the change from indirect bandgap to direct bandgap with the change of MoS_2 layer thickness. Some of the important factors in the fabrication of various MoS_2 devices are the precise control of the layer thickness and the n/p doping on the MoS_2 layer surface. In this study, using atomic layer etching (ALE) method, MoS_2 layer thickness was precisely controlled and the characteristics of the MoS_2 heterojunction devices fabricated by the ALE methods were investigated. Also, using the precise ion bombardment energy used for the anisotropic ALE, the surface sulfur on MoS_2 was preferentially removed and/or replaced with nitrogen, and their material properties and device characteristics were also investigated. This presentation will show some potential applications of ALE techniques for next generation devices using 2D materials including graphene, MoS_2, $MoSe_2$, etc.

9:55am **LI-ALE-WeM3-6 Structural and Compositional Evolution of SiN Surfaces Under Low Energy Ar^+ Bombardment***, **Erik Cheng**, G. Hwang,* University of Texas at Austin*; P. Ventzek, Z. Chen,* Tokyo Electron America

In ALE of many materials, a low energy ion bombardment step is critical for achieving etch. The nature of the nonequilibrium chemistry happening under such conditions, however, has not yet been thoroughly examined. In this talk, we present our recent work utilizing density functional tight binding (DFTBMD) simulations to elucidate the underlying mechanisms governing the substrate-precursor-ion interactions in the ALE of silicon nitride (SiN) and the resulting film structure and composition. We have found that in the absence of adsorbed precursors, surfaces of all conditions (N-rich, Si-rich, amorphous, crystalline) tend to converge towards an amorphous Si-rich surface with many coordination defects. The Si:N ratio at the surface, which starts around 75%, linearly increases to 82% after 20 bombardments on a 15Å × 15Å surface, while the surface defect density grows from 0% to around 30%, with a predicted saturation around 50% based on a power law fit. The formation of this quasi-equilibrium structure can largely be attributed to the sputtering of H and N-containing moieties being strongly favored over the sputtering of Si-containing moieties. In the presence of an adsorbed monolayer, sputtering can be suppressed, but largely shows the same trends. Interestingly, in the presence of a fluorocarbon monolayer, relatively few N-C and Si-F bonds are formed, suggesting that reaction pathways for this process may not be in line with previously thought. Furthermore, the highly damaged surfaces due to ion bombardment have been seen to be far less reactive than previously expected. In this talk, we will also discuss the underlying reasons for these peculiar behaviors.

10:10am **LI-ALE-WeM3-9 Demonstration of Atomic-Layer-Etching of SiO_2 in a small-plasma-volume incorporating 162MHz CCP source and 27MHz substrate bias using CHF_3 and Ar/O_2***, **Cleo Harvey**, B. Ellingboe,* Dublin City University, Ireland

Atomic-scale-processing control of SiO_2 is one of the main requirements to achieve nanoscale device fabrication. Here, we demonstrate a self-limiting Atomic-Layer-Etching process of SiO_2 in a large-area dual-frequency CCP using cyclic CHF_3 and Ar/O_2. The plasma reactor is a modification of an industrial low-volume CCP for 300mm wafer processing. The original upper grounded electrode is replaced with a multi-tile array excited differentially at 162MHz. Ion-energy is controlled via 27MHz power coupled to the electro-static-chuck and wafer. The ALE process involves alternating gases and VHF excitation for cyclic fluorocarbon deposition and etch-back. The unique plasma chemistry and low-energy sheath of high-VHF limits ion-driven surface mixing; this in turn promotes an etch plateau resulting in a broader process window with a fully-self-limiting removal half-cycle. In this study, we present the effect of VHF and LF power coupling on plasma parameters in the dual-excited reactor; namely electron density from hairpin probe, relative radical species density from OES, and ion energy effects inferred from sputter rates. The results provide insight into the operational window and favourable conditions to realise ALE behaviour in our experimental system. Thickness changes are measured by an in-vacuo Phase-Modulated-Spectroscopic-Ellipsometer (PMSE) and further validated in an ex-situ commercial ellipsometer. The atomic composition and chemical bonding structure of the deposited layers and the surface following etch-back are analysed by x-ray photoelectron spectroscopy (XPS). Following fluorocarbon deposition, etch-back thickness changes plateaus after 30 seconds, demonstrating fully-self-limiting removal process, and producing an etch-per-cycle of 0.4-0.5nm/cycle. Optical emission tracking of the CO etch by-product signal exhibits a decay and plateau time consistent with the active-etch-period. Surface composition of the SiO_2 surface after several cycles of ALE by XPS does not show evidence of a carbon-rich (such as C-C bond) residue.

10:25am **LI-ALE-WeM3-12 Vacuum Ultraviolet Enhanced Atomic Layer Etching of Metal Films***, **Xin Yang**, H. Nallan,* University of Texas at Austin*; B. Coffey,* Lam Research*; J. Ekerdt,* University of Texas at Austin

Electroless Cu deposition is widely applied in nanofabrication processes as it can be incorporated into roll-to-roll processing and operated at low temperatures for flexible electronics. Cu patterns can be created using a base or noble metal catalyst (Pd, Ru, etc.) since the electroless deposition only happens where the catalyst is present. These patterns are used in flexible display technologies, such as transparent conductive electrodes. Since Cu nucleates on all catalyst present, fine control over catalyst growth regions is critical. Area selective atomic layer deposition (AS-ALD) is explored to create catalyst patterns. However, a shortcoming that AS-ALD suffers is finite selectivity, which leads to metal nucleation in undesired regions. We present an atomic layer etching (ALE) process to remove undesired metal clusters/islands after AS-ALD growth without significantly affecting the metal film thickness.

Low-temperature, plasma-free ALE of Pd, and Ru is demonstrated. Etching of Pd and Ru is achieved at 50 – 200 °C, with approximate material removal rates of 2.8 and 0.9 Å/cycle, respectively, which is characterized *in situ* using X-ray photoelectron spectroscopy and *ex situ* using X-ray reflectivity. The metal film/islands are co-exposed to vacuum ultraviolet (VUV) light ($115 < \lambda < 400$ nm) and O_2 gas at 1 Torr for 2 – 5 min in the oxidation half-cycle. The amount of metal oxide formed in the near surface region can be controlled by the co-exposure time and substrate temperature. In the etch half-cycles, formic acid vapor is used to remove the metal oxides that formed without etching zero-valent metal. Atomic O is the main species responsible for oxidation from VUV/O_2 co-exposure. Density Functional Theory modeling of atomic O interaction with the metals and diffusion into the metals is discussed. The flux of atomic O is important in the oxidation process to overcome the energy barrier to subsurface O diffusion, which limits the depth of oxidation. ALE of continuous and discontinuous Pd films is presented to illustrate how VUV - ALE can be used to remove undesired metal growth due to differing oxidation behavior between those two films. Specifically, we observe a minimum of 3 min is required to partially oxidize a 20 nm uniformly thick film, while a 2 nm film is fully oxidized after 3 min at same substrate temperature. This variation is likely due to the different exposed surface areas. This could be exploited to remove materials in undesired regions after or during area-selective metal ALD under mild thermal conditions.

Keywords: atomic layer etching, atomic oxygen, vacuum ultraviolet photons, metals

10:50am **LI-ALE-WeM3-17 Plasma ALE for Anisotropic and Isotropic Etching***, **Erwin Kessels**, A. Mackus,* Eindhoven University of Technology, Netherlands **INVITED**

Plasmas provide the unique ability to etch materials through chemical and physical processes that can be tuned by the choice of plasma gases and the level of ion bombardment. For anisotropic etching, most ALE processes rely on a chemically inert Ar plasma in which the energetic ions remove the modified surface layer in a directional manner. Plasmas can also be used for isotropic ALE when the plasma is used to create chemically reactive neutral species (plasma radicals) under conditions in which ion bombardment is negligible. Under such circumstances, the ALE process can benefit from the high and diverse reactivity that can be obtained by plasmas enabling a wider range of etch chemistries than thermal ALE processes. Moreover, when using plasma-based processes, it is also possible to switch easily between anisotropic and isotropic etching which might be of interest for advanced feature control and other innovative etch processes that can become of interest.

In this presentation, two recent innovations will be discussed, one related to anisotropic ALE and one for isotropic ALE. For anisotropic ALE, very precise ion energy control through the so-called tailored-waveform biasing method will be presented. Although this method was first reported two decades ago, recently dedicated power supplies have become commercially available which is now being used in ALE processes [1]. The key advantage of this method that it leads to very narrow energy distributions for ion energies that can be precisely tuned between 20 and 200 eV such that chemical and physical sputtering thresholds can be probed and such that it is easier to work exactly in the ALE ion windows.For isotropic ALE, results will be presented as achieved by using a F-based plasma for the etching of oxides instead of HF. More in particular, isotropic ALE of Al_2O_3 will be demonstrated using a processes based on SF_6 plasma exposure and $Al(CH_3)_3$ dosing [2]. It will be demonstrated that this process yields higher etch rates and lower processing temperatures than thermal ALE.

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11:10am **LI-ALE-WeM3-21 Atomic Layer Etching of Gallium Nitride (Gan) Using SF_6/Ar Plasmas***, **Lamiae Hamraoui**, T. Tillocher, P. Lefaucheux, R. Dussart,* GREMI CNRS/Université d'Orléans, France*; M. Boufnichel,* STMicroelectronics, France

Due to its excellent electrical properties, Gallium nitride (GaN) is a promising semiconductor for the next generation of high-power devices as for example, the normally-off high electron mobility transistors (HEMTs). Plasma etching of GaN is involved in the fabrication of such components but damages the material and degrades its electric properties. Hence, there is a high interest in the atomic layer etching (ALE) processes, which are expected to provide high precision and damage-free etching.

So far, most of the research activity carried out on GaN ALE, has been performed using chlorine based chemistry for the modification step. The idea is to form $GaCl_3$, which is a quite volatile etch by-product [1], [2]. Fluorinated chemistries for ALE of GaN have also been studied to a lesser extent. For example, some authors have used a CF_4/O_2/Ar plasma mixture for the modification step in order to etch GaN [3]. Another team has reported on XeF_2 reactants in the modification step of a thermal ALE process to create the modified layer at the surface [4].

In this work, an SF_6 plasma is proposed for the modification step of GaN ALE. This process consists of cyclic SF_6 plasma chemisorption step and Ar plasma removal step. SF_6 plasma enables to form a layer of GaF_3. This etch by-product is non-volatile and has a boiling point as high as 1000 °C at atmospheric pressure [5]. The GaF_3 modified layer can be removed during the etching step under the effect of Ar^+ ion bombardment. Since the Ar^+ ion energy is adjusted so that unmodified GaN under-layers are not sputtered, self-limiting etching (SLE) can be achieved whereas the modified layer is depleted.

Tests were performed in an inductively coupled plasma (ICP) reactor. The influence of several parameters such as gas flow rates, modification and removal step times and bias voltage has been investigated. The etch depth and the surface roughness were measured using AFM.

GaN etched depth per cycle (EPC) increases slowly with the SF_6 exposure duration. After 100 cycles, we measured an average EPC as low as 0.1 nm/cycle, which shows that less than a monolayer is etched per cycle in these particular conditions.

This work is supported by the European Union (IPCEI) and Région Centre through the Nano2022 project. The CERTeM 2020 platform has provided most of the equipment.

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11:25am **LI-ALE-WeM3-24 Selective Atomic Layer Etching between GaN and SiN by Using HBr Neutral Beam***, **Takahiro Sawada**, D. Ohori,* Tohoku University, Japan*; K. Sugawara,* Sumitomo Electric Industries, Ltd., Japan*; M. Okada, K. Nakata, K. Inoue,* Sumitomo Electric Industries, Ltd, Japan*; D. Sato,* Showa Denko K.K., Japan*; S. Samukawa,* Tohoku University, Japan

AlGaN/GaN high electron mobility transistors (HEMTs) are promising for both high-power and high-frequency applications because their two-dimensional electron gas (2DEG) has high saturation velocity, high mobility, and high carrier concentration with a high breakdown field. However, in GaN HEMT structures for 5G communications, it has been pointed out that damage during the etching process in the recess gate process is causing the degradation in device performance and reliability. In the recess gate etching process, the SiN insulating film on the cap layer should be etched, but it is necessary to etch only the SiN layer and eliminate the etching of underlaying GaN layer. Namely, an atomic layer etching with defect-free and reasonable SiN/GaN etching selectivity is required. In this study, we investigated higher selective etching between SiN and GaN using HBr neutral beam (NB) and found that it exhibited a more selective reaction compared to Cl_2 NB.

The etching rate of GaN mainly depended on the desorption rate of the etching product ($GaCl_x$ or $GaBr_x$) assisted by the bombardment of NB. As a result, in the case of the HBr neutral beam, the GaN etching rate was drastically decreased at the atomic layer level because the vapor pressure of the etching product, $GaBr_x$, was much lower than that of $GaCl_x$. On the other hand, the dominant etching progression of SiN was mainly caused by neutral beam bombardment energy, and the desorption of the etching products ($SiCl_x$ or $SiBr_x$) was almost the same in both cases because the vapor pressures of the etching product, $SiCl_x$ and $SiBr_x$. Especially, in the case of the HBr neutral beam, the neutral beam energy dependence of the surface reaction layer of SiN was larger than that of Cl_2 NB. As a result, the etching selectivity between SiN and GaN in HBr NB improved to 2.1 at 10 W of bias power, whereas that with Cl_2 NB was saturated at 0.41 at more than 10 W of bias power. We found that the surface atomic layer etching reaction could precisely control the desorption rate of the etching product by optimizing the neutral beam bombardment energy and gas chemistry. The HBr neutral beam process can achieve atomic layer level selective reactions on the SiN/GaN structure.

11:40am **LI-ALE-WeM3-27 Study of Surface Damage Formation in Atomic Layer Etching of Si via Molecular Dynamics Simulation***, **Erin Joy Capdos Tinacba**, M. Isobe, S. Hamaguchi,* Osaka University, Japan

Etching of materials in atomic scale can provide a precise and highly controllable means to form nano-scale structures on a material surface. The atomic scale precision is especially desirable in etching of stacked materials such as those in self-aligned contacts. Such an etching process can be achieved by atomic layer etching (ALE), which has been widely studied to counter the challenges in manufacturing of ever-shrinking electronic devices in the semiconductor industry. A typical plasma enhanced ALE process is divided into two steps [1]. The first is the adsorption step, where a thin layer of the material's top surface is modified by the deposition of highly reactive species. In the case of silicon (Si), a chlorine (Cl) plasma is typically used to supply Cl radicals to the surface, as Cl is known to diffuse less deeply into the bulk material. The second is the desorption step, where the modified Si layer is etched by non-reactive energetic ions (e.g., Ar^+ ions) supplied by another plasma. Ideally, it is expected that no or very low damage is formed on the processed material surface by low-energy ion bombardment during the desorption step. However, there have been few published studies on the surface characterization of Si after ALE etching. In this study, molecular dynamics simulation was employed to examine the ALE of Si with Cl radicals in the adsorption step and Ar^+ ions in the desorption step. Effects of low and high Cl radical and Ar^+ ion doses as well as Ar^+ ion energy (20 to 60 eV) on the etch per cycle (EPC) and surface damage were studied. The simulated EPC, 1.55 Å/nm, with low Cl radical dose (~0.14×10^{16} radicals/cm^2) and 20 eV Ar^+ ion energy is consistent with available experimental data [2].

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12:00pm **LI-ALE-WeM3-31 Patterning High Density STT-MRAM with a Novel Atomic Layer Etch Process**, ***Samantha Tan**, W. Yang, T. Mukherjee, Z. El Otell, Y. Fan, R. Lin, S. Yun, K. Kanarik, T. Lill, Y. Pan, R. Gottscho,* Lam Research Corporation **INVITED**

Spin-Torque transfer magneto resistive random-access memory (SST-MRAM) has the benefits of a comparable integration density of DRAM and performance of SRAM, with its intrinsic characteristic of non-volatility, high endurance, and long retention time. STT-MRAM can directly be coupled with processors while simultaneously used as non-volatile storage, thus plays a variety of on-chip memory role in advanced VLSI technology.[1] However, SST-MRAM stacks are challenging to pattern since the stacks mainly consist of non-volatile ferromagnetic materials such as Co, Fe, Pt. Conventional reactive ion etch usually induces chemical damage to magnetic tunnel junction (MTJ) layers, which limits electrical performance.

Thermal ALE concept has recently been demonstrated to expand the pathway to chemically etch magnetic metals.[2] The process typically consists of two steps, oxidation or halogenation followed by ligand or organic vapor exposure to form volatile byproduct. J. Chang demonstrated a surface modification assisted organic chemical vapor etch for directional and isotropic etch of magnetic and noble metals, also developed a comprehensive framework for selecting viable chemistries.[3] R. Opila demonstrated Co thermal ALE with a sequential exposure to Cl_2 and hexafluoro acetylacetone and its molecular mechanism.[4]

Here, we developed a plasma assisted chemical etch approach for Co that forms volatile etch by-product. Based on the chemical etch mechanism, we developed a novel atomic layer etch process for STT-MRAM patterning. Combining the novel etch chemistry, ALE takes the advantages of process control that minimizes MTJ damage with minimum I/D loading. This breakthrough on the etch process enables tight pitch MRAM patterning not only for embedded MRAM, but also for standalone memory.

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12:20pm **LI-ALE-WeM3-35 Exploring Thermal Ale for Spin-Torque Majority Gate Applications**, ***Jean-Francois de Marneffe**,* imec v.z.w., Belgium*; P. Nguyen,* Air Liquide*; S. Couet, L. Souriau,* imec v.z.w., Belgium*; N. Stafford, P. Venkateswara,* Air Liquide*; S. De Gendt,* imec v.z.w. / KULeuven, Dpt of Chemistry, Belgium*; Y. Canvel,* imec v.z.w, Belgium

The spin-torque majority gate (STMG) [1] device is a competitive option for beyond-CMOS logic computing, enabling high density at low power consumption. In such a system, the information is stored in magnetic domain walls, i.e. interfaces separating regions with different magnetization direction. Based on quantum 'exchange' interactions between electrons, the domain walls propagate, interact, and the majority magnetization direction dominates. The majority gate device itself consists of a cross-shaped free layer that is common to 4 magnetic tunnel junctions (3 inputs, 1 output, all consisting of a so-called reference magnetic layer). The magnetization direction of the 3 'input' free layers is switched using spin transfer torque, by flowing a current through each of the magnetic tunnel junctions. The output state is measured by tunneling magnetoresistance. Amongst multiple manufacturing challenges, the etching of the magnetic tunnel junction is the most difficult, as it requires to etch pillars containing non-volatile metals and land selectively on the MgO tunnel barrier, which is 1nm thick. To reduce damage to the MgO, the development of soft-landing options is essential. In the current paper, the thermal atomic layer etching of CoFeB is studied, by means of a cycling process combining first surface chlorination, followed by reaction with hexafluoroacetylacetone (hfacH) [2]. This soft-landing process demonstrates efficient removal of Co, Fe and B, and good selectivity to the underlying MgO dielectric. The impact of the process on the perpendicular magnetic anisotropy is also studied.

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12:35pm **LI-ALE-WeM3-38 Topographic Selective Deposition (TSD) by Combining Plasma Enhanced Atomic Layer Deposition and Atomic Layer Etching Processes**, ***Moustapha Jaffal**, G. Lefevre, T. Yeghoyan, T. Chevolleau,* LTM, France*; R. Gassilloud, N. Posseme,* CEA-LETI, France*; M. Bonvalot,* LTM, France*; C. Vallee,* University Grenoble-Alpes, France

Topographic selective deposition (TSD) processes are attracting a strong interest in the advanced manufacturing of increasingly complex semiconductor devices [1]. For spacer definition, TSD can be obtained from a conformal deposition process on pitches and three-dimensional (3D) nanostructures using Plasma Enhanced Atomic Layer Deposition (PEALD), followed by a subsequent anisotropic etching process step of top and bottom deposits, in order to keep only vertical coatings on 3D feature sidewalls [2].This TSD route thus eliminates numerous and costly wafer-handling steps during the fabrication process and also avoids detrimental Edge Placement Errors (EPE) due to inherent limitation of photolithography[3;4].

In this work, we investigate a strategy for depositing spacers using an original super-cycle process route, composed of a Ta_2O_5 standard PEALD deposition whereby cycling is intercalated by Atomic Layer Etching (ALE) process steps. The ALE process consists first of a CF_4/H_2 plasma chemical treatment and second of an *in situ* anisotropic low energy Ar^+sputtering step of chemically modified Ta_2O_5 horizontal surfaces. This Two-step ALE process mitigates 3D substrate damages induced by energetic ion bombardment such as amorphization and horizontal surface roughness.

The optimization of both PEALD and ALE process steps has first been carried out on planar native Si substrates. It has then been transferred to 3D structures and led to a TSD on vertical sidewalls, as shown in Figure 1. This talk will outline the optimization strategies that we have developed for TSD and discuss the advantages and shortcomings of such a process. Special attention will be dedicated to cross contamination issues raised by the fluorine-rich ALE step.

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12:50pm **LI-ALE-WeM3-41 Surface Smoothing by Atomic Layer Deposition and Etching**, *S. Gerritsen, **Nicholas Chittock**, V. Vandalon, W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

In striving to produce smaller nanoelectronic devices ever thinner films are needed, which increasingly requires control of film roughness and line edge/width roughness. ALD and ALE processing have separately been observed to reduce the roughness of surfaces.[1,2] In this work, the mechanisms of surface smoothing by ALD and ALE are investigated, and the application of ALD + ALE for surface smoothing is discussed. The increased use of ALD and ALE provides the opportunity to better control the surface roughness while maintaining ultrathin film thicknesses.

Previous studies reporting on ALD/ALE smoothing effects ascribe the smoothing to conformal deposition/etching. In our work finite difference simulations were performed that model ALD/ALE as a uniform front from which the deposition/etching propagates isotropically at every point (similar to Huygens–Fresnel principle in optics). These simulations illustrate enhanced deposition in valleys due to geometrical constrains and the rounding of sharp peaks, together leading to a reduction in small scale roughness.

The smoothing effect described by the uniform front propagation model was validated by AFMmeasurements of Al_2O_3 films prepared by ALD from TMA/O_2 plasma and isotropic ALE from TMA/SF_6 plasma.[3]For ALD excellent agreement was seen, but comparatively faster smoothing was observed for ALE, which reveals that a second mechanism contributes to the smoothing. The enhanced smoothing for ALE is explained by considering that the fluorination of the film depends on the local curvature, corresponding to a higher concentration of fluorine at peaks and a lower concentration in valleys.

An extended model that includes both uniform front propagation and curvature-dependent fluorination showed good agreement between simulation and experimental results. This extended model enabled the evaluation of different strategies for using ALD + ALE to smoothen surfaces. The benefits of combining ALD + ALE to smoothen surfaces will be discussed, showing that significant smoothing can be obtained for relatively thin films.

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1:05pm **LI-ALE-WeM3-44 In Situ Analysis on Atomic Layer Etching of Al_2O_3*, Johanna Reif***, *M. Knaut, S. Killge, M. Albert, J. Bartha, T. Mikolajick,* Technische Universität Dresden, Germany

Controlled thin film etching is essential for future semiconductor devices, especially with complex high aspect ratio structures. Atomic layer etching (ALE) is a technique that can remove materials precisely with atomic layer control based on sequential, self-limiting surface reactions. ALE is considered to be one of the most promising techniques for achieving the low process variability at atomic-scale. In this work, the thermal ALE (tALE) process to etch Al_2O_3 using TMA as the metal precursor for ligand exchange and HF as the fluorination reactant was examined. For an in situ and real-time access to the etch process, the process chamber was equipped with a spectroscopic ellipsometer. Spectroscopic ellipsometry (SE) has widely served as a powerful non-invasive method to monitor time-continuous as well as time-discrete atomic scale processes in situ and even in real-time. While the ALE process modifies chemical compositions of the surface through a material removal, SE can observe these changes in the electronic structure of the surface in situ and in real-time. The SE measurements enabled the study of etch characteristics in dependence of process parameters like pulse time, process pressure, and substrate temperature. Additional, the utilized reactor was clustered to an ultra-high vacuum analytic system for direct surface analysis like X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). The combination with a non-destructive analytic system provided unadulterated information about the chemical composition and roughness during the process. The high sensitivity of these measurements allowed investigations of interface reactions even for a single ALE pulse as well as analysis of the initial etch mechanism. Our studies observed linear thickness decrease versus the number of ALE cycles during the tALE process. The etch per cycle (EPC) increased from 0.92 Å/cyc at 50 Pa to 1.31 Å /cyc at 200 Pa. The fluoride thickness was observed to increase with process pressure, resulting in more etching during the ligand-exchange reaction with TMA. We investigated the transition between AlF_3 ALD at lower process temperatures and Al_2O_3 ALE at higher temperatures. The EPC varied from -0.4 Å/cyc at 200 °C to +1.38 Å/cyc at 350 °C. Additional analysis demonstrated the self-limiting behavior of the surface reactions. Furthermore, we examined the initial-stage etch of Al_2O_3 using in vacuo XPS measurements. In our presentation, we will show in detail that the combination of in situ and in vacuo studies leads to a better understanding of the ALE process and the reaction mechanism in the sub monolayer regime during tALE.

1:20pm **LI-ALE-WeM3-47 Announcement of ALE and ALD Student Awardees, Closing Remarks & Thank Yous***, A. Raley,* TEL Technology Center, America, LLC*; S. Hamaguchi,* Osaka University, Japan*;* ***Thorsten Lill,*** Lam Research Corp.

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

ALD Applications

Room On Demand - Session AA1

Energy: Catalysis and Fuel Cells

AA1-1 High-crystalline RuO_2based on Atomic Layer Deposition for Oxygen Evolution Catalyst, ***Jaehyeok Kim**, D. Kim, J. Park, H. Kim,* Yonsei University, Korea

To alternate carbon-based energy source to protect the nature, hydrogen is widely researched worldwide. Electrochemical water splitting is the promising method that produces no pollutant, only $H_2$and O_2. However, Oxygen Evolution Reaction (OER) is sluggish, which determines the overall efficiency of electrocatalyst, so that water splitting is limited in industrial field.

RuO_2has been researched as efficient catalyst for oxygen evolution. The crystallinity of the RuO_2affects the efficiency. Therefore, synthesis of high-crystalline $RuO_2$is important. To enhance the efficiency of RuO_2, large surface-to-volume ratio and controllability of the crystallinity are the key factors in synthesis method.

Atomic Layer Deposition (ALD) has advantages of excellent conformality, large-area uniformity, and precise controllability of the thickness. For efficient catalyst, large surface area is helpful because it is directly related to the reaction sites. ALD is suitable fabrication process for electrocatalyst.

In this report, RuO_2film was synthesized based on ALD on Carbon Fiber Paper (CFP) at different growth temperature, which has large surface-to-volume ratio with high conductivity. It can be directly used for OER catalyst with enlarged active sites of OER. For the analysis, material properties of ALD RuO_2 such as X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, SiO_2substrate was prepared as reference. Electrochemical properties was measured in 3-electrode system consists of working electrode, reference electrode, and counter electrode. It showed low overpotential and Tafel slope, which imposes promising candidate for OER catalyst.

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AA1-2 Atomic Layer Deposition of Pt@Pd Core-Shell Structure Electrocatalyst for Carbon Dioxide Reduction, ***Ming Li,*** Delft University of Technology, China*; R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Using electrocatalysts to convert CO_2 into chemicals or fuels through electrochemical reactions is an attractive approach to reduce CO2 emissions and decrease the greenhouse effect. However, existing electrocatalysts have several technological limitations, such as low selectivity, poor stability, low conversion rates of the feedstock, and high overpotential which will lead to energy losses. Most of the electrocatalyst improvement strategies focus on catalyst structure and composition optimization such as nanostructuring, doping and alloying, etc. However, the widely used catalyst fabrication methods, like impregnation, colloidal, ion-exchange methods are tough to tailor the morphology of the catalyst down to the atomic scale, let alone other delicate structures like nano-sized core-shell particles. One promising solution is to use the atomic layer deposition method to fabricate electrocatalysts with well-defined nanostructure. It is reported that Pd-Pt bimetallic catalyst can reduce CO_2 toward formic acid and achieve a high faradic efficiency at room temperature and atmospheric pressure. We investigate whether the performance of this catalyst could be further improved by tuning the nanostructure of the catalyst with ALD. We studied how to use fluidized bed ALD to synthesize core-shell structure bimetallic electrocatalysts, and synthesized the Pd-Pt bimetallic catalyst with core-shell structure on carbon black substrate in this work. The metal loading of the catalyst is precisely controlled. TEM, XPS, XRD, SEM, and ICP-OES were used to characterize the catalyst structure and metal loading. Electrochemical measurements were carried out in a custom-made H-cell using a three-electrode assembly at room temperature. This gives us a better understanding of the effect of the catalyst structure on carbon dioxide reduction, helping us to come to an optimized structure and the corresponding ALD strategy to make it.

AA1-3 Understanding Metal-Support Interactions in Model Pd/ALD-Al_2O_3/SiO_2 Catalysts, ***Arun Asundi**, E. Goodman,* Stanford University*; A. Hoffman,* SLAC National Accelerator Laboratory*; K. Bustillo,* Lawrence Berkeley Lab, University of California, Berkeley*; J. Stebbins,* Stanford University*; S. Bare,* SLAC National Accelerator Laboratory*; S. Bent, M. Cargnello,* Stanford University

The synergy between coexisting metal and metal oxide phases is critical in determining the reactivity of many supported heterogeneous catalysts. The interaction between the active metal and the support is one example of this synergy and can be controlled to modulate catalyst performance. ALD offers a unique opportunity to study metal-support interactions by enabling support modification one atomic layer at a time. Metal-support interactions are readily apparent in Pd methane combustion catalysts, where support properties can affect reaction rate by several orders of magnitude. Previous work has shown that the methane combustion rate is significantly higher for Pd/Al_2O_3 than Pd/SiO_2, but the nature of the metal-support interaction that determines this reaction rate is not well-understood. In this work, we study the effects of support chemical properties and morphology on the methane combustion reactivity of Pd supported on ALD Al_2O_3-modified SiO_2.

Catalysts were prepared through a combined ALD and colloidal synthesis method. Uniform SiO_2 nanospheres were modified with different thicknesses of Al_2O_3 films deposited by ALD. Colloidal Pd nanocrystals were then deposited on the ALD-Al-$_2$O$_{3--}$/SiO_2 supports. This synthesis method enabled independent control over the Pd nanocrystal size, Pd loading, and chemical nature of the support. The transition of the support properties from SiO_2 to Al_2O_3 results in two regimes of improved reactivity as a function of Al_2O_3 ALD cycle number: the reaction rate increases rapidly at low Al_2O_3 coverage and increases gradually at high Al_2O_3 loading. The two stages of promotion show that both surface and bulk properties of Al_2O_3 are important factors in controlling the reaction rate. At sub-monolayer alumina coverage, the reaction rate is determined by the number of Pd/Al interface sites. Through infrared spectroscopy we show that a monolayer of Al_2O_3 is deposited during the first three ALD cycles, leading to a linear increase in reaction rate as a function of ALD cycle number as the support surface transitions from SiO_2 to Al_2O_3. At high Al_2O_3 loadings, bulk properties of Al_2O_3 such as purity and crystallinity also affect reaction rate. ^{27}Al nuclear magnetic resonance spectroscopy reveals intermixing between Si and Al and crystallization of the Al_2O_3 for sufficiently thick coatings, both of which modulate the methane combustion rate. This work demonstrates the many support characteristics that influence catalyst reactivity through metal-support interactions. The controlled ALD-colloidal synthesis method used in this work can be applied to fundamental studies of metal-metal oxide interactions in many catalyst systems.

AA1-4 Size Control of Gold Nanoparticles Using Sequential Atomic Layer Deposition of Gold and Titanium Dioxide, ***Saeed Saedy**, R. Baaijens,* Delft University of Technology, Netherlands*; E. Goodwin, M. Griffiths, S. T. Barry,* Carleton University, Canada*; J. van Ommen,* Delft University of Technology, Netherlands

Gold nanoparticles (AuNPs) supported on metal oxides exhibit exceptional catalytic activities in several processes, especially oxidation reactions. The performance of AuNPs strongly depends on size. Large gold particles do not show notable catalytic activity; the lack of efficient synthesis and stabilization methods of AuNPs resulted in gold being considered a catalytically inactive metal for decades. Additionally, due to weak interaction with the supports, the supported GNPs usually are not stable enough and tend to agglomerate, again resulting in activity loss.

This strong dependency of catalytic activity imposes a significant obstacle in developing supported AuNPs as catalysts, especially when the AuNPs with an average size smaller than 5 nm are desired. This challenge becomes more significant when the preparation of large amounts of supported AuNPs is the final goal, which is the prerequisite of practical applications. For such applications, the supported AuNP synthesis method needs to be capable of controlling the AuNPs size, scaling to large-scale production, and reproducibility. The conventional AuNP syntheses are a variety of liquid phase methods, which have been widely studied for decades; however, they still suffer from poor size control, contamination of the final product with residual solvents/co-reactants, reproducibility issues, and high sensitivity to operating conditions.

Atomic layer deposition (ALD) has proven successful for the synthesis of supported metal NPs for various applications, especially as catalysts. ALD makes it possible to synthesize supported NPs with controlled size, shape, and morphology. Recently we reported ALD synthesis of supported AuNPs on TiO-$_2$ in a fluidized bed reactor, with the minimum average particle size of 4 nm. In this work, we report a modification to our previous synthesis, enabling us to attain Au/TiO_2 with an average particle size of 2.8 nm. In this method, a sequential ALD of metallic gold (using trimethylphosphinotrimethylgold(III)), TiO_2 (using isopropoxytitanium (IV)), and ozone (as an oxidizer) at 105°C were used to confine the ALD deposited AuNPs with a TiO_2 over-coat. Different TiO_2:Au pulse ratios from 1 to 4 were used. An analysis by inductively coupled plasma optical emission spectrometry of the resulting samples showed a gold loading of about 0.8% in samples. Transmission electron micrographs indicated a decrease of AuNP average size from 3.7 nm to 2.8 nm. Interestingly, the particle size distribution became narrower with increasing the TiO_2:Au pulse ratio. The standard deviation of AuNP size decreased from 1.4 nm to 0.8 nm.

AA1-7 Atomic Layer Deposition for Improved Biomass Conversion Catalysts*, **Wilson McNeary**, S. Tacey, G. Lahti, D. Conklin,* National Renewable Energy Laboratory*; K. Unocic,* Oak Ridge Natinal Laboratory*; E. Tan,* National Renewable Energy Laboratory*; E. Wegener,* Argonne National Laboratory*; T. Eralp Erden,* Johnson Matthey, UK*; S. Moulton, C. Gump, J. Burger,* Forge Nano*; M. Griffin, C. Farberow,* National Renewable Energy Laboratory*; M. Watson, L. Tuxworth,* Johnson Matthey, UK*; K. van Allsburg,* National Renewable Energy Laboratory*; A. Dameron, K. Buechler,* Forge Nano*; D. Vardon,* National Renewable Energy Laboratory

Heterogeneous catalysts are a key enabler of the transition towards a sustainable, bio-based economy for fuels and chemicals. However, the harsh conditions in many biomass conversion processes lead to nanoparticle sintering, support collapse, and metal leaching in conventional PGM catalysts. Next-generation catalysts must be developed to address these stability challenges. This presentation will discuss ongoing work between the Catalytic Carbon Transformation and Scale-Up Center at NREL and various industrial partners to develop scalable and cost-effective atomic layer deposition (ALD) coatings for improving the performance of biomass conversion catalysts.

The substantial focus will be devoted to the benefits of TiO_2 ALD coatings on supported Pd hydrogenation catalysts. Ten cycles of TiO_2 ALD were found to dramatically improve the activity of a conventional Pd/Al_2O_3 catalyst towards aromatic hydrogenation, despite partial coverage of the Pd sites by the ALD layer. Subsequent advanced characterization and atomic-scale computational modeling revealed that the ALD coating weakened the adsorption strength of hydrogenation surface intermediates, leading to higher reaction rates. Reaction testing after exposure to sulfur impurities, high temperature oxidation, and hydrothermal treatment demonstrated the improved stability of the ALD-coated catalyst. Additionally, the ALD synthesis process was found to be scalable over two orders of magnitude with minimal deviation in synthesized catalyst properties. These results were contextualized with cost models of industrial ALD coating and aromatic hydrogenation processes to further refine the value proposition of ALD coatings. Given the demonstrated improvements in hydrogenation, TiO_2 ALD coatings have also been applied to supported Pt catalysts for use in other biomass conversion reactions, such as hydrodeoxygenation for the production of sustainable aviation fuel (SAF) and the oxidation of glucose to bio-derived gluconic acid. Recent findings from these experimental campaigns will also be shared. ALD technology holds great potential in the development of next-generation catalysts for biofuels and bioproducts, and this work constitutes an important examination of the impact of ALD coatings in a variety of reaction environments.

AA1-10 Electrochemical Activation of Atomic Layer Deposited Cobalt Phosphate Electrocatalysts for Water Oxidation*, **Gerben van Straaten**, R. Zhang, V. DiPalma,* Eindhoven University of Technology, Netherlands*; G. Zafeiropoulos,* Dutch Institute For Fundamental Energy Research, Netherlands*; E. Kessels,* Eindhoven University of Technology, Netherlands*; R. van de Sanden, M. Tsampas,* Dutch Institute For Fundamental Energy Research, Netherlands*; A. Creatore,* Eindhoven University of Technology, Netherlands

Storage of electricity into chemicals is the most viable answer to the intermittency of renewable sources and the most investigated example this is water splitting. For the O_2 evolution half reaction (OER), cobalt phosphate-based electrocatalysts (CoPi) are interesting as they are made of earth-abundant elements and their catalytic activity scales with film thickness. In parallel with others[1], we have demonstrated synthesis of amorphous CoPi films by ALD [2]. CoPi is prepared by combining ALD of CoO_x from cobaltocene ($CoCp_2$) and O_2 plasma, with cycles of TMP ($(CH_3O)_3PO$) and O_2 plasma, according to an ABCD recipe scheme [2,3]. We have also shown that tuning the Co-to-P ratio, by combining this recipe with extra cycles of CoO_x, enhances the OER performance [3], beyond that achieved by traditional electro-deposited films.

In the present contribution we focus on the mechanism behind the enhancement of the catalytic activity of CoPi when tuning the Co-to-P ratio. We show that ALD CoPi thin films undergo activation with increasing number of cyclic voltammetry (CV) cycles. During this activation process, the current density increases in parallel with a progressive leaching of phosphorous out of the electrocatalyst and the shift of the oxidation state of Co from Co^{2+} to a mixture of Co^{2+} and Co^{3+} [4]. This induce structural changes in the electrocatalyst: CV combined with Rutherford backscattering indicate that after activation, for the best performing CoPi film, as much as 22% of all Co atoms become accessible to the electrolyte. Measurements of the electrochemical surface area (ECSA) reveal that during activation, the ECSA of this film increases by a factor 30. However, this increase in ECSA is strongly dependent on the initial composition of the CoPi films. While the aforementioned increase holds for CoPi films with a Co-to-P ratio of 1.6, for films with a Co-to-P ratio of 1.9 the ECSA only increases by a factor 3.6. We find that for all investigated Co-to-P ratios, after activation the electrochemical activity scales linearly with ECSA. Thus, the initial composition affects the activity of the catalyst indirectly by guiding the restructuring of the catalyst during potential cycling and the ECSA is a critical parameter in determining the activity of CoPi-based and related electrocatalysts. Thus, next to the well-established control over film properties ALD of CoPi enables to disclose the mechanisms behind its electrochemical activation.

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ALD Applications
Room On Demand - Session AA10
Memory Applications: RRAM & Neuromorphic, MIM Capacitors

AA10-1 Li-Nb-O Family Deposited by Atomic Layer Deposition (ALD) for Artificial Neuron and Synapse*, **Hyun Seung Choi**, H. Kim, S. Park, T. Park,* Hanyang University, Korea (Republic of)

Neuromorphic computing, consisting of artificial neurons and synapses, is one of the most promising candidates to resolve the von-Neumann bottleneck because of its in-memory-computing attributes, high efficiency, and parallel signal processing. Recently, artificial neurons and synapses have been studies using the variety of materials to improving device properties. The lithium niobium oxide (Li-Nb-O) family have many desirable multifunctional properties including memory, TS behavior, ferroelectric effect, etc. [1-2] Among these properties, niobium oxide (NbO_2) is well known as metal-insulator-transition selector, and lithium niobate ($LiNbO_x$) as memristor. [3] Especially, lithium niobate can represent superior characteristics due to small ion size of lithium (Li) ion enabling low energy consumption, high mobility, and high endurance. Despite the potential for new and enhanced functional devices and materials, this Li-Nb-O multifunctional family remains relatively unexplored due to the difficulty of precise composition control.

In this study, niobium oxide and lithium niobate deposited by Atomic Layer Deposition (ALD) are proposed for artificial neuron and synapse. Controllable memory and TS behaviors are confirmed by adjusting the composition of Li-Nb-O compound. Niobium oxide represented the volatile property as reported, and lithium niobate showed analog switching memory applicable to artificial synapse. Especially, by understanding the effect of Li-ion concentration on synaptic properties such as potentiation/depression, an optimal composition of lithium niobate is achieved. Consequently, our work can provide an easy yet effective way to construct functional neuromorphic devices by using similar materials in same family.

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**AA10-2 Li Compound-Based Two-Terminal Artificial Synaptic Devices via Atomic Layer Deposition*, Hye Rim Kim,* *H. Choi, S. Park,* Hanyang University, Korea (Republic of)*; G. Kim ,* Korea Research Institute of Chemical Technology (KRICT), Korea (Republic of)*; T. Park,* Hanyang University, Korea (Republic of)

Brain-inspired neuromorphic computing is considered a novel computing paradigm that mimics the human brain, capable of parallel data processing and low power consumption. [1] Memristor devices are potential candidates as a synaptic component for neuromorphic computing especially towards spiking neural networks (SNN) due to their inherent nature. [2] Lithium titanate ($Li_4Ti_5O_{12}$, LTO) as a proposed anode material of lithium (Li) ion batteries, is a zero-strain material capable of reversible Li ion migration. Also, the feasibility of synaptic characteristics in lithium titanate based device has been confirmed through the metallic and insulating phase separation by an electric field. [3] The behavior of Li ions, a key component of synaptic properties, is highly dependent on the Li concentrations inside the LTO active layer [4], but related studies are still insufficient.

In this research, the lithium titanate active layers were grown through atomic layer deposition (ALD) and fine composition control was achieved using super-cycle method. Sequentially, the Li concentration-dependent resistive switching characteristics of the LTO based memristor devices were confirmed. Also, synaptic properties including potentiation and depression were confirmed by applying the identical neuronal spikes. Consequently, we derived an optimized Li concentration of the lithium titanate materials suitable for synapse devices using atomic layer deposition and pulse engineering. The detailed experimental results will be presented.

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ALD Applications
Room On Demand - Session AA11
Memory Applications: Other Non-Volatile Memories (MRAM, FeRAM, Phase Change,...)

**AA11-1 Fabrication of Vertical-Type Phase-Change Memory Leveraging Atomic Layer Deposition*, Jeong Woo Jeon,* *C. Yoo, E. Park, W. Kim, W. Choi, B. Park,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

Storage Class Memory (SCM) is a new hybrid storage/memory tier to achieve high speed, low power computing using a nonvolatile and byte-accessible memory denser than DRAM and faster and more durable than flash memory.[1] Intel and Micron Technology recently commercialized the SCM using chalcogenide-based phase-change memory (PCM) that utilizes resistance contrast between the amorphous and crystalline states for data storage. It has stacked memory cell arrays that alternately share either wordlines or bitlines between the different memory layers. This structure inevitably requires lithography and patterning steps proportional to the number of layers, resulting in high production costs. For the commercial success of PCM-based SCMs, it is important to achieve high density and low cost per bit, which requires the development of a novel three-dimensional (3-D) architecture similar to the 3-D vertical-NAND device.

This report demonstrates the vertical-type PCM (V-PCM) enabled by atomic layer deposition (ALD) of $Ge_2Sb_2Te_5$ (GST-225), as shown in Fig. 1.[2] SiO_2 was used for interlayer dielectric (ILD) separating each memory layer, and TiN was used for the bottom electrode (BE). Fig. 1(b) shows an ALD GST-225 films conformally grown on vertically etched sidewalls, in which ILD and BE are alternately stacked. The switching region is defined by the patterned width and thickness of the BE, equivalent to the structure of a mushroom type cell vertically erected. In this work, the contact area was as high as 0.02 mm^2 due to the limited lithography capability of university scale research. The electrical characteristics of the fabricated device can be seen in Fig. 2. The SET and RESET characteristics of the V-PCM device are shown with a threshold voltage of 1.4 V and a RESET current of 4 mA, which corresponds to a RESET current density of 20 MA/cm^2. The cyclic endurance was more than 10^8 cycles, which is sufficiently high compared with the planar type PCM devices, showing the feasibility of the ultra-high density V-PCM.

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**AA11-2 Effect of Ti Scavenging Layer on Ferroelectricity of $Hf_xZr_{1-x}O_2$ Thin Films Fabricated by Atomic Layer Deposition using Hf/Zr Cocktail Precursor*, Takashi Onaya,* Meiji University/National Institute for Materials Science/JSPS Research Fellow, Japan*; T. Nabatame,* National Institute for Materials Science, Japan*; N. Sawamoto,* Meiji Renewable Energy Laboratory, Japan*; A. Ohi, N. Ikeda, T. Nagata,* National Institute for Materials Science, Japan*; A. Ogura,* Meiji University/Meiji Renewable Energy Laboratory, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) films have attracted a lot of attention for ferroelectric field-effect transistor (FeFET) applications. Numerous papers have reported that an annealing process at > 300°C is required to obtain the ferroelectric orthorhombic (O) phase. [1] However, an interlayer such as SiO_x between an HZO film and a Si substrate was typically formed during the fabrication process of metal-ferroelectric-semiconductor (MFS) structures and an annealing process. To understand how the fabrication process affects the interlayer formation is important because the interlayer can cause reliability problem and reduction in remanent polarization ($2P_r$). We employed a Ti layer deposited on an HZO film because Ti can scavenge oxygen from a SiO_x interlayer. [2] In this work, we studied the effect of an annealing temperature on the interlayer formation and ferroelectricity of HZO-based MFS capacitors with a Ti layer.

A 10-nm-thick HZO film was deposited on a p^+-Si substrate by atomic layer deposition at 300°C using $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf:Zr = 1:1) cocktail precursor and H_2O gas. Next, a 1-nm-thick Ti layer was deposited on an HZO film by DC sputtering. A 100-nm-thick TiN top-electrode was then fabricated by DC sputtering. Finally, a post-metallization annealing (PMA) was performed at 300 or 400°C for 1 min in N_2 ambient. TiN/HZO/p^+-Si capacitors were also fabricated as references.

For the MFS capacitor without a Ti layer, the SiO_x interlayer could be formed between an HZO film and a Si substrate after the PMA at 400°C while the formation of the interlayer was found to be negligible, evaluated by X-ray photoelectron spectroscopy. The 300°C-PMA-treated MFS capacitors showed almost the same capacitance (C) of 0.8 $\mu F/cm^2$ regardless of the presence of a Ti layer. After the PMA at 400°C, on the other hand, the higher C was obtained because HZO films were crystallized with the ferroelectric O phase. Moreover, the MFS capacitors with a Ti layer exhibited slightly higher C of 1.5 $\mu F/cm^2$ than that (1.3 $\mu F/cm^2$) without a Ti layer. This might be attributed to the reduction of the interfacial SiO_x layer due to the scavenging effect of a Ti layer. [2] Therefore, the higher $2P_r$ value (33 $\mu C/cm^2$) of the MFS capacitor with a Ti layer was achieved compared to that (26 $\mu C/cm^2$) without a Ti layer. Based on these results, inserting a Ti layer could be one of the pathways to improve ferroelectricity of HZO films in MFS structures.

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**AA11-3 Atomic Layer Deposition of Antiferroelectric La-Doped $Hf_{0.5}Zr_{0.5}O_2$ Thin Film and Its Electrical Behaviors*, Yong Chan Jung,* *J. Kim, S. Hwang, J. Mohan, H. Hernendez-Arriaga,* University of Texas at Dallas*; W. Maeng, K. Im,* SK hynix Inc, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

Recently, the ferroelectricity and antiferroelectricity of doped Hf-based fluorite-structured ferroelectric thin films have been extensively investigated. In particular, it has been reported that La-doping for $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films can be applied to stabilize the ferroelectric orthorhombic (O) phase ($Pca2_1$) if the low doping concentration is precisely controlled.[1] On the other hand, ferroelectric-antiferroelectric transition is shown when the amount of La doping is relatively large due to its amorphizing characteristic for HfO_2,i.e. increase of crystallization temperature.[2] For the antiferroelectricity of HZO, it is known as the nonpolar tetragonal ($P4_2/nmc$) is contributed, however, it is less clear than the ferroelectric O phase.

In this study, we investigated the doping effects of La on the antiferroelectric properties of the HZO film. The HZO film as a reference was deposited on the TiN bottom electrode by atomic layer deposition (ALD) using TDMA-Hf, TDMA-Zr, and O_3 as the precursors of Hf, Zr, and oxidant, respectively. To dope the HZO film with La, $La(^iP_rfAMD)_3$ and O_3 were used as the La precursor and oxygen source, respectively. The 10-nm thick La-doped HZO film (LHZO) growth was proceeded with 6 super cycles consisting of 8 (Hf-purge-O_3-purge-Zr-purge-O_3-purge) and 1 ($La(^iP_rfAMD)_3$-purge-O_3-purge). In Figure 1, the Hf, Zr, and La concentration of the LHZO film is 48, 48, and 4 at. % as confirmed by XPS depth profiling. After the TiN top electrode was deposited on HZO and LHZO films, rapid thermal annealing was done, and metal-insulator-metal capacitors were fabricated using a Pd/Au hard mask and wet etch process.

In Figure 2(a) and 2(b), the small-signal dielectric constant of LHZO film at 0 MV/cm was increased to 69 compared to 48 of HZO film and the leakage current density of LHZO film at 1 MV/cm was approximately 2 order magnitude lower than HZO film, respectively. We suspected that the higher dielectric constant and lower leakage current is caused by tetragonal phase in the LHZO film. In Figure 3(a), the ferroelectric-antiferroelectric transition of the LHZO film was proved by the polarization-electric field curves, the remnant polarization ($2P_r$) of HZO and LHZO devices is 56 and 5 μC/cm^2, respectively. As shown in Figure 3(b), interestingly, after 10^8 and 10^9 endurance cycling, the $2P_r$ of the LHZO film is recovered to 13 and 26 μC/cm^2, respectively. It is plausible to suggest that this phenomenon is occurred due to the field-induced ferroelectric phase transition[3] or the effect of domain unpinning after longer switching cycles with high electric field (2.5 MV/cm).

This work is supported by SK hynix Inc.

AA11-4 Metal-insulator Transition in ALD VO_2 using VCl_4 and H_2O as Precursors, *Jeya Prakash Ganesan*, *D. Dev, A. Krishnaprasad,* University of Central Florida; *D. Moser, R. Kanjolia,* EMD Electronics; *T. Roy,* Nanoscience Technology Center, University of Central Florida; *P. Banerjee,* University of Central Florida

Vanadium dioxide (VO_2) undergoes a reversible transition between the semiconducting (monoclinic) and metallic (tetragonal) state at 68 °C, thus making VO_2 a perfect candidate for electrical/optical switches, thermal sensors, metamaterials, and oscillators. Atomic Layer Deposition (ALD) of VO_2 has been reported with different metalorganic and halide-based vanadium precursors. Out of these, the halide-based precursors have the advantage of a simpler chemistry, high vapor pressure and ease of delivery, little or no potential carbon residue and use of milder oxidants such as, H_2O.

In this talk, we demonstrate the ALD of VO_2 using VCl_4 and H_2O in a VEECO® FIJI Gen2 ALD system. The as-deposited films are amorphous and turn crystalline VO_2 only after a post-deposition anneal at 550 °C, 60-minute using forming gas. Raman spectroscopy is used to confirm the amorphous nature of the film pre-anneal, and its conversion to monoclinic VO_2 post-anneal. X-ray photoelectron spectroscopy suggests that the as-deposited film and the annealed film show vanadium oxides with mixed valence states on the surface and VO_2 in the bulk. Thus, despite using a V^{4+} precursor significant surface oxidation takes place during deposition to produce a multivalent oxygen-rich surface. The excess surface oxygen could result in an amorphous film. Temperature-dependent Raman spectroscopy and ellipsometric studies reveal the semiconducting to metallic transition (SMT) of annealed and crystallized VO_2 thin film. The transition temperature is recorded at 68 °C for a 30 nm film. Optical constants (*n, k*) from ellipsometry suggests that beyond 68 °C, significant free carrier absorption in the near infrared results in higher *k*. Electrical measurements performed on a fabricated device showed SMT behavior at 68 °C with a resistance high (semiconducting) : low (metallic) ratio of 66.

In conclusion, we have deposited 30 nm VO_2 via ALD using VCl_4 and H_2O at 350 °C. Contrary to a past report,[1] the VO_2 deposited in the current work is amorphous and must be annealed at 550 °C for 60 minutes in forming gas to obtain VO_2 films with SMT properties. Experimental investigations are currently underway to understand the synthesis-structure-property relationship in this promising ALD chemistry such that as-deposited, crystalline VO_2 films can be reliably obtained.

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ALD Applications
Room On Demand - Session AA12
Display Applications: Thin Film Transistor, Diodes, Thin Film Encapsulation for OLEDs/QDs...

AA12-1 Two-dimensional electron gas at atomic-layer-deposited ZnS/ZnO Heterostructure, *Jae Hyun Yoon*, *T. Seok,* Hanyang University, Korea (Republic of); *Y. Liu,* Hanyang University, China; *J. Choi, S. Kim, T. Park,* Hanyang University, Korea (Republic of); *S. Lee,* Ajou University, Korea (Republic of)

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to its presence at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial LaAlO3/single-crystal SrTiO3 (LAO/STO) heterostructure shows high density of electrons (~10^13-10^14 cm^-2) confined at the oxide interface, where the density is about ~100 times higher than that of a typical semiconductor interface (~10^11-10^12 cm^-2).[1] Creation of 2DEG is conventionally defined on the basis of discontinuity in polarity linked with the difference in the charge of the atomic layers. Simply, it can be described as half an electron charge being transferred to the interface to avoid a potential divergence, 'polar catastrophe'.[2] Another mechanism is associated with the generation of oxygen vacancies (Vo) at the surface of the STO layer during LAO or Al2O3 layer deposition, acting as electron donor for the 2DEG formation. It provides an opportunity for 2DEG realization for various oxide heterostructures and fabrication processes. Recently, we reported Vo generation mechanism-based 2DEG formation process using atomic-layer-deposited (ALD) ultrathin (~10 nm) binary metal oxide heterostructure.[3] 2DEG layer can be formed at the interface of an ultrathin Al2O3/TiO2 heterostructure on standard SiO2 substrate at a low temperature

AA12-2 Three-Dimensional Multi-Stacked Field-Effect Transistor Using Two-Dimensional Electron Gas at the Interface ofAl_2O_3/ZnO Ultra-Thin Film Heterostructures, *Ji Hyeon Choi*, *T. Seok, J. Yoon,* Hanyang University, Korea; *S. Lee,* Ajou University, Korea (Republic of); *T. Park,* Hanyang University, Korea

Two-dimensional electron gas (2DEG) has been realized with various fabrication process using diverse oxide heterostructure since epitaxial $LaAlO_3$/single-crystal $SrTiO_3$ (LAO/STO) heterostructure was reported as a typical 2DEG system, which shows high density of electrons (~10^{13}-10^{14} cm^{-2}) confined at the oxide interface. The origin of 2DEG created at the heterointerface is still controversial mainly between the discontinuity of polarity at the atomic layers, inducing electron charge reconstruction and the presence of oxygen vacancies (V_o) at the interface, widely known as electron donors. Recently, we reported V_o generation mechanism-based 2DEG formation process using atomic-layer-deposited (ALD) ultrathin (~10 nm) binary metal oxide heterostructure: amorphous Al_2O_3/polycrystalline TiO_2, whose electrical property is comparable with typical LAO/STO epitaxial 2DEG system at room temperature (sheet carrier density, n_{sh}= ~10^{14} cm^{-2}, electron mobility, μ_n= ~4 cm^{2}V^{-1}s^{-1}). To demonstrate V_o generation mechanism for 2DEG creation specifically, an *in-situ* resistance measurement was conducted to prove the presence and effect of V_o at the heterointerface. The resistance of the interface dropped significantly with the injection of trimethylaluminum (TMA) molecules, indicating that V_o were formed on the TiO_2 surface during the TMA pulse in the ALD of the Al_2O_3 film, such that they provide electron donor states to generate free electrons at the interface of the Al_2O_3/TiO_2 heterostructure, creating 2DEG. Being well-informed of this mechanism, ZnO as a different bottom material was applied for oxide heterostructure 2DEG system to improve electrical and structural property of TiO_2-based 2DEG due to its excellent intrinsic property. As expected, the Al_2O_3/ZnO heterostructure exhibited enhanced electrical properties (n_{sh}= ~10^{14} cm^{-2}, μ_n= ~15 cm^{2}V^{-1}s^{-1}), even at the lower thickness of bottom layer (~ 5 nm) and lower deposition temperature (150°C).

In this work, using ultrathin Al_2O_3/ZnO 2DEG layer as a channel, we succeeded to fabricate 2DEG field-effect transistors (FETs), achieving extremely low off-current (I_{off} ~10^{-9} A/m), high on/off current ratio (I_{on}/I_{off} > ~10^9), and low subthreshold swing (SS ~95 mV/dec.), which outperforms other oxide heterostructure-based FETs reported so far, including the previous work of TiO_2-based 2DEG system.Furthermore, due to facile film deposition with excellent thickness control of ALD, stacking 2DEG layers is possible to make three-dimensional multi-stacked 2DEG FETs, leading to great conductivity resulting from accumulated electron transport path. The detailed experimental results will be presented.

AA12-3 Atomic Layer Deposited p-type SnO Thin Film Transistors*, Kham Niang*, *D. Gomersall,* Cambridge University, UK*; J. Parish, A. Johnson,* University of Bath, UK*; A. Flewitt,* Cambridge University, UK

In the past decade, extensive research has been carried out on p-type oxide semiconductor materials for realisation of complementary metal oxide semiconductor (CMOS) circuits. In particular, SnO is of great interest due to its disperse valence band maximum due to hybridization between O 2*p* and Sn 5*s* orbitals, allowing a relatively high hole mobility [1]. While sputtering method has been widely used for SnO, atomic layer deposition (ALD) has not been widely reported [2]. ALD is a very attractive technique due to its precision on stoichiometry arising from the self-limiting growth, its repeatability and its conformality over a large substrate area [3].

In this report, SnO thin films were deposited using a novel Sn precursor and H_2O in a cross-flow wafer scale ALD reactor. The precursor bottle was heated at 100°C and depositions were carried out at temperatures between 170 and 210°C. To achieve high quality films suitable for channel layers in thin film transistors (TFTs), we investigated three deposition modes: single pulse (SP), multiple pulses (MP) and multiple pulses and exposure (MP+E). The SP mode is the standard ALD process comprising of the Sn and H_2O half cycles. The pulse/purge times of 1s/15s and 0.03s/10s are used for the Sn and H_2O cycles respectively. In the MP mode, three consecutive Sn pulses are applied with 5 s delay between the pulses which is then followed by the H_2O half cycle. The MP+E mode is a combination of the MP mode and stopping of the gas flow for 10s to increase the residence time in the chamber.

P-type SnO thin films were then incorporated as a channel layer in TFTs. A field effect mobilities of 0.5 and 2.5 $cm^2V^{-1}s^{-1}$ were achieved for TFTs annealed at 250°C and 350°C respectively. We will discuss in detail the effect of different ALD deposition modes on the characteristic of the thin films and the performance of the TFTs.

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AA12-4 The Impact of PEALD InGaO TFT Performances on Paring In/Ga Precursor Structures*, TaeHyun Hong*, *H. Jeong, J. Park,* Hanyang University, Korea

Recently, ALD oxide semiconductor has been attractive as TFT material that has the potential for high mobility and stability compared to conventional method due to precisely controlled thickness and metal composition. However, multi-component deposition using ALD is difficult to control without understating growth mechanism according to precursor and reactant, it is necessary to study and library the adsorption and reactivity of the surface depending on various precursor. In this study, InGaO (IGO) semiconductors were deposited by plasma enhanced atomic layer deposition (PEALD) using two sets of In and Ga precursors, which one set is $In(CH_3)_3[CH_3OCH_2CH_2NHtBu]$ (TMION) and $Ga(CH_3)_3[CH_3OCH_2CH_2NHtBu])$ (TMGON) and the other is $(CH_3)_2In(CH_2)_3N(CH_3)_2$ (DADI), $(CH_3)_3Ga$ (TMGa), as denoted as TM-IGO and DT-IGO, respectively. We changed the ratio of InO sub-cycles from 3 to 19 to control the chemical composition of ALD-processed films. The different growth properties are observed at different precursor set. This could be originated from the precursor structure and the density of adsorption sites. Despite this different growth behavior, it could set the IGO TFTs with the identical In/Ga ratio controlling each super-cycle. Interestingly, the both TFTs (TM-IGO and DT-IGO) showed different film properties and the associated TFT characteristics (TM-IGO: -5.5V, 36.7 cm^2/Vs, DT-IGO: -9.7V, 27.7 cm^2/Vs for the V_{th} and mobility respectively). This difference could be originated from not only the growth behavior but also the anion/cation ratio/binding states in the IGO thin films.

AA12-5 Structural Modulation of ALD IGZO TFT for Controlling the Hydrogen Concentration*, Wan-Ho Choi*, *K. Kim, J. Park,* Hanyang University, Korea

Nowadays, a novel deposition technique for thin film transistor (TFT) application using atomic layer deposition (ALD) such as semiconductor, gate insulator (GI), and encapsulation has been studied extensively. Herein, we developed unified-ALD (U-ALD), which deposits buffer, semiconductor and GI by ALD and named this structure as sandwich structure. In U-ALD IGZO TFTs, material forming interfaces with the channel layer exhibited a critical role in the electrical performance of IGZO TFTs because of hydrogen (H) diffusion, which has a Janus-faced effect in IGZO. Through measurement of hydrogen permeability of ALD insulators and Secondary Ion Mass Spectroscopy of each sandwich structure after annealing, we found a hydrogen accumulation effect in the ALD IGZO layer like a dam, which caused degradation of TFT properties. In contrast, TFTs with ALD SiO_2, which has proper hydrogen diffusivity, chosen as the buffer and GI had favorable electric properties of 28.17 cm^2/Vs, 0.20 V/decade, 0.96 V, and 0.12 V for the mobility, V_{th}, SS, and hysteresis. In this regard, an optimized GI structure via the ALD SiO_2 and Al_2O_3 in situ process on the basis of excellent interface formation with the semiconductor and hydrogen barrier performance, respectively, was developed. This functional GI structure with SiO_2 and Al_2O_3 exhibited proper TFT characteristics (27.52 cm^2/Vs, 0.24 V/decade, and 1.07 V for the mobility, SS, and V_{th}, respectively) and improved stability against hydrogen annealing, which was used to examine the resistance to external hydrogen.

AA12-6 Ultrathin Amorphous Titanium Oxide Field-Effect Transistors with Large Gate-Induced Electron Mobility Modulation*, Nikhil Tiwale*, Brookhaven National Laboratory*; A. Subramanian,* Stony Brook University*; Z. Dai,* Brookhaven National Laboratory*; S. Sikder,* Stony Brook University*; J. Sadowski,* Brookhaven National Laboratory*; C. Nam,* Brookhaven National Laboratory/Stony Brook University

Recent reports show a great promise of using ultrathin metal oxide films prepared by atomic layer deposition (ALD) for enabling high performance devices featuring ultra-sharp subthreshold swing and even the formation of two-dimensional electron gas (2DEG). A key characteristic of ultrathin metal oxide thin-film transistors (TFTs) is their very low off-state current with a sharp and high on off ratio. While the on-off operation in typical TFTs primarily results from the modulation of gate-dependent charge carrier density, recent reports suggest that the high on-off ratio in ultrathin oxide TFT operation can be associated with a large gate-induced carrier mobility modulation, which few reports provide a clear picture regarding its origin and implication. In this study, we study the 3.5 nm-thick amorphous-titania-based ultrathin TFT fabricated by low-temperature ALD, which exhibited six-decade on-off ratio predominantly driven by the same magnitude of gate-induced mobility modulation [Tiwale et al., *Commun. Mater.***1**, 94 (2020)]. We observe that the power law dependence of gate-dependent saturation mobility featured a very high exponent at low gate voltages, unprecedented for oxide TFTs reported so far. Drawing parallels from the disordered organic TFT that exhibits similarly high power law exponent, and by combining the physicochemical analysis of titania prepared under varying post-ALD thermal treatments and the accompanying TFT device characterization, we identify that the large gate-induced mobility modulation originates from the variable range hopping (VRH) transport of charge carriers through the band-tail states of ultrathin titania, with its bi-exponential density of states reflected on the observed two different power-law exponent regimes in the gate-dependent mobility. The results highlight rather unusual and counterintuitive roles of defect states within ultrathin metal oxides in possibly enabling some of the high performance parameters in associated TFT devices, as best exemplified by the increased off-state current accompanied by the reduced device on–off ratio upon the oxidative annealing of ultrathin titania, against the typical notion that such an oxidative annealing in metal oxide transistors would reduce the background carrier density while increasing the on–off ratio.

ALD Applications
Room On Demand - Session AA14
Emerging: Optics/Optoelectronics/Metamaterials/Plasmonics

AA14-1 Optical Quantizing Structures in Al_2O_3/TiO_2 Heterostructures by Plasma Enhanced Atomic Layer Deposition*, Pallabi Paul,* *A. Szeghalmi,* Friedrich Schiller University Jena, Germany

Atomically thin heterostructures and superlattices are promising candidates for various optoelectronic and photonic applications. In this research, different combinations of Al_2O_3/TiO_2 composites are fabricated by plasma enhanced atomic layer deposition (PEALD). The growth, dispersion relation, optical bandgap and composition of such structures are systematically studied by means of UV/VIS spectrophotometry, spectroscopic ellipsometry (SE), x-ray reflectometry (XRR), scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS). Besides, an effective medium approximation (EMA) approach is applied to model the heterostructures theoretically. The refractive index and the indirect bandgap of the heterostructures depend on the ratio of the two oxides, while the bandgap is very sensitive to the thicknesses of the barrier and quantum well layers. A large blue shift of the absorption edge from 400 nm to 320 nm is obtained by changing the TiO_2 (quantum well) thickness from ~ 2 nm to ~ 0.1 nm separated by ~ 2 nm of Al_2O_3 (barrier) layers. PEALD unfolds the possibility of achieving optical quantizing effects within complex heterostructures enabling control of their structures down to atomic scale. It enables a path towards atomic scale processing of new 'artificial' materials with desired refractive indices and bandgap combinations by precise control of their compositions.

Selected compositions are identified for applications in antireflection coatings at 355 nm wavelength. Interference multilayers of TiO_2/Al_2O_3 composites as high refractive index material and SiO_2 as the low refractive index show low reflectance and optical losses at 355 nm wavelength with transmittance values of approximately 99%. Such heterostructures overcome the limitations of the low bandgap dielectric TiO_2 for optical applications in the UV spectral range.

AA14-2 Excellent Surface Passivation of Germanium by ALD Al_2O_3 with a-Si:H Interlayers, ***Willem-Jan Berghuis***, *J. Melskens, B. Macco, R. Theeuwes, K. Erwin,* Eindhoven University of Technology, Netherlands

After the adoption of ALD for the preparation of high-k gate oxides in field-effect transistors (FETs), the unique features of ALD have only become more important with the advancement of the technology nodes: precise and uniform thickness control, excellent conformality, and the ability to generate high-quality surfaces with well-passivated channel surface states. For the next-generation, multiple stacked nanosheet FETs, the requirements become even more stringent. Now the gate needs to be wrapped all around the channel while also both Si and Ge channel surface states need to be passivated. Similar challenges lie in the passivation of Ge and SiGe nanowire devices such as nanolasers, nano-LEDs, and solar cells.

The passivation of SiGe and Ge surfaces by ALD films has been a long-standing challenge which mostly has been addressed by examining FET-like structures. We have recently carried out an in-depth study of the passivation of Ge by ALD Al_2O_3 films. By measuring the carrier lifetime on passivated substrates we extracted the maximum effective surface recombination velocity $S_{eff,max}$. For Al_2O_3, we demonstrated that values as low as $S_{eff,max}$= 170 cm s^{-1} can be achieved after optimization of the ALD substrate temperature, film thickness, and post-deposition anneal temperature. It was moreover established that a GeO_x interlayer forms during ALD and that the GeO_x/Al_2O_3 stack on a Ge surface has a negative fixed oxide charge density ($Q_f = - 1.8\cdot10^{12}$ cm^{-2}).

In this work, we have systematically examined the surface passivation of Ge by thermal and plasma-enhanced ALD Al_2O_3 in combination with an amorphous silicon (a-Si:H) interlayer. For this purpose, we have grown a-Si:H/Al_2O_3 stacks on Ge substrates under various conditions using plasma-enhanced chemical vapor deposition (PECVD) for the a-Si:H layer (1-10 nm) and ALD for the Al_2O_3 (5-20 nm). We found an excellent surface passivation by an a-Si:H layer as thin as 1.7 nm ($S_{eff,max}$ = 6.8 cm s^{-1}). To better understand the role of the a-Si:H interlayer and its interaction with the ALD Al_2O_3 film, we have performed measurements of the interface defect density (D_{it}) and fixed charge density (Q_f) together with a Transmission Electron Microscopy study. We have found a remarkably high fixed charge ($Q_f = - 8.8\cdot10^{12}$ cm^{-2}) present in this passivation stack due to the interplay between the Si and PEALD Al_2O_3 leading to a SiO_x interlayer making it a Ge/a-Si:H/SiO_x/Al_2O_3 stack. Thermal ALD Al_2O_3 yields a lower $Q_f$in comparison, which is likely related to a less prominent SiO_x interlayer. The understanding of this material system is expected to be valuable for the design of well passivated Ge interfaces and devices.

AA14-3 Tunable and Scalable Fabrication of Plasmonic Dimer Arrays With Sub-10 nm Nanogaps by Area Selective ALD, ***Chengwu Zhang***, *B. Willis,* University of Connecticut

Plasmonic nanoantennas, especially with sub-10 nm nanogaps, can greatly enhance electric fields through excitations of surface plasmons, which are collective oscillations of electrons excited by light.Arrays of plasmonic nanoantennas can be designed to concentrate and manipulate light at the nanoscale, and have wide applications such as surface enhanced spectroscopy, photo-driven chemical conversion, and optical information processing.Atomic layer deposition (ALD) is a thin-film deposition technique capable of producing conformal thin films with precise control of thickness and composition at the atomic level.Area selective ALD (AS-ALD) provides a flexible way to precisely tune nanogaps to enhance their optical and electrical properties. In this work, we investigate the optical response of plasmonic nanoantenna dimer arrays with sub-10 nm nanogaps by AS-ALD.

We present a case study of Cu AS-ALD on Pd/Au layered nanoantenna dimers. Figure 1 shows a side view schematic diagram of AS-ALD to tune nanogaps. Pd layers are designed to promote Cu nucleation, and Au layers provide strong plasmonic resonances in the visible and near IR range. Arrays of Pd/Au layered nanoantenna dimers are fabricated on fused quartz substrates using electron beam lithography, followed by Cu AS-ALD to tune the inter-particle distances. Results show nanogaps can be well tuned to sub-10 nm. In figure 2, the nanogaps are measured by electron microscopy and the average post-ALD gap is 6.5 ± 2.2 nm. The inset shows an example dimer with a nanogap of 4.2 nm; each pixel in the SEM image is 0.9 nm. Optical extinction curves were measured to track the changes to the dipolar plasmonic resonances as the number of ALD layers was increased. Figure 3 shows the extinction measurements for light polarized along the axis of the dimer. The dipolar resonance initially blue shifts around 100 nm after 50 ALD cycles, and then red shifts back towards the pre-ALD peak location after more deposition cycles. Control experiments show that the initial blue-shift is largely due to heating, which can slightly modify the nanostructures by rounding corners and edges. Electrodynamics simulations show that additional factors include increasing thickness and decreasing aspect ratio, which also tend to blue-shift the resonances. The data show that beyond 50 cycles, the resonance red-shifts due to the dominant effect of narrowing the nanogaps, which is supported by simulations. In this way, the study shows considerable spectral "tunability" by tailoring the optical responses of plasmonic nanoantenna arrays, while creating nanogaps that concentrate electric fields for various applications.

AA14-4 Lithium Aluminum Fluoride as an Ultraviolet Coating Material*,* ***John Hennessy***, Jet Propulsion Laboratory

Optical systems operating in the far ultraviolet (90–200 nm) often employ protected aluminum mirror coatings. These mirror systems utilize protective thin films of metal fluoride materials to maintain optical transparency in the wavelength range of interest. The most common protective coating material for this application is MgF_2 which limits the short wavelength performance of the mirror to the band edge cutoff of MgF_2 at approximately 120 nm. There is growing interest for astrophysics applications in the use of LiF protective coatings which can extend the short-wavelength performance due to its larger bandgap, however the hygroscopic properties of LiF can present challenges for the stability and longevity of the final optical system. In this work, we investigate the use of atomic layer deposition to create thin films of lithium aluminum fluoride as an ultraviolet coating material. We have employed a supercycle approach utilizing LiHMDS, tris(dimethylamino)aluminum, and anhydrous HF as co-reactants at substrate temperatures between 100 and 200 °C. This chemical pathway avoids possible deleterious interactions that can occur between simple alkylaluminum precursors and alkali materials, and ultimately allows for arbitrary mixed thin film compositions ranging from purely crystalline LiF, to purely amorphous AlF_3. At intermediate supercyle ratios we also show that crystalline films of Li_3AlF_6 can be deposited with this process as confirmed by x-ray diffraction analysis. We present recent results on protected aluminum mirror coatings fabricated with this approach, along with environmental exposure testing comparing the performance of Li_3AlF_6 to LiF and AlF_3. The prospects for utilizing this approach in future NASA instrumentation will be discussed along with the possibility of using these films as battery coating materials. Crystalline films of Li_3AlF_6 are also known to possess moderate Li-ion conductivity and the low deposition temperature investigated in this work may have benefits over other ALD approaches in this material system.

AA14-7 Stress Compensated HfO_2/SiO_2 High-reflective Coatings at 355 nm and 532 nm by Plasma Enhanced Atomic Layer Deposition using Substrate Biasing, ***Vivek Beladiya***, Friedrich-Schiller-University Jena, Germany*; D. Kästner,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany*; S. Riese, P. Hanke,* LAYERTEC GmbH, Germany*; A. Szeghalmi,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany

Atomic layer deposition is a promising thin film deposition technology due to its ability to coat complex formed substrates with precise thickness control and excellent uniformity. The substrate biasing technique in plasma enhanced atomic layer deposition has recently gained attention due to its ability to manipulate material properties such as refractive index, density, residual OH impurity, residual mechanical stress, crystallinity, and surface roughness. The kinetic energy of the plasma species can be varied by applying a substrate bias potential across the plasma sheath at the substrate surface. In this work, we have deposited high-reflective (HR) coatings at 355 nm and 532 nm at 100°C deposition temperature using substrate biasing.

The multilayer system consists of HfO_2 and SiO_2 as a high and low refractive index layer, respectively, which were grown using a substrate biasing. The total film thickness of HR@355nm and HR@532nm were 1.6 µm and 2.3 µm, respectively. The total residual stress measured on double-side polished Si wafers was 76 MPa (tensile) and 112 MPa (tensile) for HR@355nm and HR@532 nm, respectively. The reflectance of 99.9 was measured using a spectrophotometer at 355 nm and 532 nm wavelengths for HR@355nm and HR532nm, respectively.Additionally, a reflectance of above 99.9 was determined at 355 nm wavelength for HR@355nm multilayer coating by means of cavity ring-down measurements. The coatings were free of delamination and visible cracks. The laser-induced damage threshold (LIDT) was performed at 355 nm using the R-on-1 method on HR@355nm multilayer coating. The LIDT of 19 J/cm^3 was observed. Hence, we have successfully demonstrated stress compensated high-reflective (HR) coatings for the designed wavelengths of 355 nm and 532 nm with excellent uniformity and mechanical stability.

ALD Applications
Room On Demand - Session AA15
Emerging: Medical/Healthcare/Pharmaceuticals

AA15-1 Atomic Layer Deposition of Nanocomposite Antimicrobial and Antiviral Coatings*, **Anil Mane**, M. Gros, R. Wilton, S. Forrester, Y. Zhang, . Zaluzec, D. Schabacker, S. Darling , J. Elam,* Argonne National Laboratory, USA

Antimicrobial (AB) and antiviral (AV) coatings can play a crucial role in health and safety by preventing the growth and spread of pathogens. Based on the chemical composition of these coatings can drastically reduce or even kill the bacterial and viruses via surface chemical reaction, catalytic reaction activated by light, thermal treatment, in presence of reactive gases or surface functional groups.Antimicrobial and antiviral-coated surfaces are becoming more broadly examined for possible use in areas such as medical clothing and equipment, surfaces encountered in public and private transportation and household use. The most common and most significant use of antimicrobial/antiviral coatings has been used in healthcare in the manufacture of masks and equipment to prevent hospital related infections, which have accounted for more than a million deaths worldwide. In addition, the current pandemic caused by the SARS-CoV-2 virus has infected more than 100 millon people resulting in over 2.2 million deaths from COVID-19. Therefore, it is essential to develop effective antimicrobial and antiviral coatings to address a wide range of needs.

Antimicrobial/viral coatings can be prepared using a variety of thin film coating processes. A thin coating can be applied to a surface that has a chemical composition which is toxic to microorganisms but not to humans. Among the various coatings, layers containing Cu and Ag have been shown particularly effective against microorganisms and viruses. In addition, other coatings such as TiO_2, ZnO and MoO_3 have also shown antimicrobial/antiviral properties. Due to outstanding processing advantages, we have evaluated atomic layer deposition (ALD) as a viable approach for the commercial production of AB/AV coatings.In this study, we prepared a wide variety of ALD materials including binary, ternary, and quaternary oxides and composites on N95 mask filter materials (polypropylene) and polyester fabrics at temperatures as low as 50ºC. All of these ALD materials showed uniform and conformal coatings that infiltrated the porous fabrics. We tested the antibacterial and antiviral properties of these ALD coated materials and identified coating formulations that were highly effective against bacteria and viruses. Moreover, the coatings did not diminish the filtration properties of the N95 mask filters.In this presentation we will discuss the coating materials, the AB/AV testing results and future directions. We think that the technology present here can be used for other air filter applications.

ALD Applications
Room On Demand - Session AA16
Emerging: Others (Protective Coatings, Hardness, MEMs...)

AA16-1 Capacitance Modulation by Light and Mechanical Stimuli in ALD-deposited ZnO Thin Films Integrated in Piezotronic MEMS Strain Microsensors*, **Raoul Joly**, S. Girod, N. Adjeroud, P. Grysan, J. Polesel,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

By the means of Atomic Layer Deposition (ALD), we developed piezotronic strain sensitive sensors integrated in polyimide cantilevers, where a zinc oxide (ZnO) thin film is deposited on top of patterned interdigitated platinum electrodes (Figure 1(a)). The rapidly spreading Internet-of-Things is accelerating MEMS (Micro-ElectroMechanical Systems) industry to deliver highly sensitive and miniaturized self-sensors with low consumption and cost-effective production process. Due to its high film conformality, low temperature processing, self-limiting nature and thickness control at the nanoscale level, ALD technique has emerged as an ideal technique to add new functionalities in MEMS.

We propose to rationalize the ALD processing deposition parameters on the sensor's electrical properties and the sensitivity of detection for mechanical strain and light. We report on the evidence of negative capacitance phenomena occurring at the interface of Schottky junctions over a wide frequency range (between 20 Hz and 100 kHz). We demonstrate an original way to modulate the sensors capacitance characteristics in the presence of a light source as well as by applying a mechanical strain to the devices (Figures 1(b), (c) and (d)). The rationale behind these observations will be discussed. The ALD thin film is made of wurtzite polycrystalline zinc oxide with a privileged (002) orientation. We optimized the deposition temperature to be compatible with microfabrication processing on polymer and photoresists by thin film growth below 100 °C. Hence, Schottky junctions are realized by microstructuring interdigitated micro-combs at the interface of high work function platinum metal electrodes and a semiconducting piezoelectric ZnO thin film. The obtained piezotronic junction has the particularity of an exponential dependence of the flowing diode current as a function of the applied mechanical strain. The sensitivity is thus greatly improved with gauge factor higher than 100.

In the last stage of this work, we will present the strain sensors size miniaturization for integration in microcantilevers in a full polymer body, compatible with AFM (Atomic Force Microscopy) scanning probe operations to highlight the very high sensitivity of detection. These results open up new perspectives and applications towards the miniaturization of highly sensitive and low power consumption environmental sensors, as well as for broadband impedance matching in radio frequency applications by the means of negative capacitance devices.

AA16-2 Applications of Atomic-Scale Processing for the Next Decade of MEMS Technology*, **Daniel Potrepka**, N. Strnad, R. Rudy,* U.S. Army Research Laboratory

Atomic-scale processing has had a major impact in the fields of microelectronics and CMOS fabrication technology, building upon the significant advances in academia. Now the field of micro-electomechanical systems (MEMS) is poised to reap the benefits of atomic-scale fabrication, as gains achieved with standard process technologies remain limited to low-cost devices. To achieve this breakthrough, ALD atomic-scale techniques will play a vital role, driving MEMS deep into the nanoscale regime by engineering innovative designs to take advantage of the scaled piezo- and ferroelectric properties encountered therein. Using a combination of ALD, ALE, and pre- and post- treatments for area-selective growth of function-enhancing features and layers, ALD can hermetically seal off devices from harsh in-process or working environments, eliminate stiction, tailor conformal multilayer geometries to provide new functionalities such as phonon crystals and metamaterials, control stress, enhance polarization and structural integrity, lower operating voltage, increase chip work density by an order of magnitude, and meet thermal, mechanical, geometrical, barrier, interface, and ferroic materials design requirements for competitive commercial MEMS technologies and devices. These breakthroughs will be enabled by a wide array of viable precursors, providing new metal oxides and metals of increasing diversity and complexity from throughout the periodic table, including the recently developed nitrides, sulfides, and tellurides [1-3]. The resulting new materials, along with rapidly occurring growth and integration of computer modeling for precursor-surface chemical reactions [4] and hardware improvements [3] will enhance the scale and pace of MEMS modernization.

ALD commercial infrastructure and equipment sales, currently predicted to increase to about USD $2 billion in 2026 at a compound annual growth rate from 2020 of 26.3% can leverage off the larger MEMS global market. Impacts of the key atomic-scale processes that can fuel this exciting expansion of the MEMS technology arena will be reviewed, emphasizing the benefits for the future of prototyping and scaled fabrication in commercial, industrial, and defense applications.

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AA16-3 Texture Control of Piezoelectric Aluminum Nitride Grown by Atomic Layer Deposition for 3D Microelectromechanical Systems*, **Nicholas Strnad**, W. Sarney,* CCDC Army Research Laboratory*; G. Rayner,* Kurt J. Lesker Company, Inc.*; G. Fox,* Fox Materials Consulting, LLC*; R. Rudy, J. Pulskamp,* CCDC Army Research Laboratory

3D microelectromechanical systems (3D-MEMS) are an emerging application space for piezoelectric films grown using ALD. ALD provides an ideal solution for the deposition of piezoelectric materials on trench sidewall or 3D fin structures which may be used to improve the size, weight, power and frequency tunability of MEMS devices. Aluminum nitride is a technologically relevant material for piezoelectric MEMS due to its significant piezoelectric response, high breakdown voltage and large mechanical quality factor. AlN is amenable to film growth by ALD, although there are relatively few reports of ALD AlN used for MEMS due to the need for additional process development to meet stringent crystal structure, film purity and grain orientation requirements for device performance. We explore several strategies for controlling the grain orientation of ALD-grown AlN on planar substrates, which includes the use of {111}-textured Pt as a growth template, precursor chemistry and dose variation, stress-engineered substrates, inductively-coupled plasma conditions for film bombardment during growth, and ALD equipment modifications. For select cases, we report the mechanical Q, determined from measurements of MEMS resonator structures, and piezoelectric coefficients, determined from measurements on MEMS cantilevers, of ALD deposited AlN . We analyze the Pt-AlN interface properties primarily by using TEM with EDS. The baseline ALD AlN process yielded completely c-axis oriented aluminum nitride as determined by x-ray diffraction, and a rocking curve full-width half max of 2.9° was achieved. The relative dielectric constant was measured to be 8.1 < K < 8.6 and an average dielectric loss of < 1% was observed within the an applied electric field range of +/- 3350 kV/cm (+/- 35 V across 104 nm thick AlN) at 10 kHz. The leakage current of the textured AlN was quite low at 1.5 x 10^{-6} A/cm^2 over the applied field range of +/- 1820 kV/cm (+/- 19 V across 104 nm thick AlN).

AA16-4 Electrically-Conductive Kevlar Fabrics for Multi-Functional Fiber Reinforced Composites Enabled by Atomic Layer Deposition*, **Robin E. Rodríguez**, T. Lee, Y. Chen, T. Cho, C. Huang, E. Kazyak, A. Poli,* University of Michigan, Ann Arbor*; W. LePage,* University of Michigan - Ann Arbor*; M. Thouless, M. Banu, N. Dasgupta,* University of Michigan, Ann Arbor

Multi-functional composites have wide-ranging applications from structural batteries to electronic devices, which are of increasing interest in the aerospace community. To operate as a device, at least one constituent of the composite needs to be electrically conductive. Polymer-matrix composites (PMCs) are generally electrically insulating and often necessitate the inclusion of electrically-conductive additives, but such additives tend to affect the bulk mechanical properties of the final product. A method to impart electrical conductivity without affecting the bulk mechanical properties of the composite is to modify the surface of the reinforcement by adding a thin, conductive coating. Among the coating techniques that can be utilized, atomic layer deposition (ALD) provides unparalleled conformality in coating of the 3-D fiber template, as well as sub-nanometer resolution in film thickness and composition.

In this work we demonstrate the fabrication of electrically-conductive Kevlar-reinforced PMCs without measurably affecting the bulk material properties, by coating Kevlar fabrics with aluminum-doped zinc oxide (AZO) via ALD. The core-shell fabric morphology and structure were characterized by SEM, XPS, and XRD. The conductive properties of the AZO-coated Kevlar fabric were measured using the four-point probe method, which were taken at the single-fiber, single-tow, and fabric level, after varying the thickness of AZO from 80-200 nm. For all the cases, the electrical resistivity decreases as the film thickness increases. The thickness-dependence of the electrical resistivity is well described by an analytical model, which allows for predictive design. These fabrics are sufficiently conductive to serve as an electrode material in textile-based devices ranging from thin-film electronics to energy storage devices.

Additionally, we studied the relationships between electrical conductivity and mechanical deformation of AZO-coated Kevlar fabrics as used in a PMC. The electrical resistance of the composite was continually monitored *in situ,* while loading the sample to failure in a tensile load frame. The ultimate tensile strength and Young's modulus of the Kevlar-reinforced PMC was not significantly affected by AZO interface coatings, illustrating the advantage of this approach over bulk conductive additives. Furthermore, changes in the electrical resistance at higher strains were observed, which is attributed to the cracking of the AZO coating. These results demonstrate the potential of AZO-coated Kevlar to make electrically conductive composites with applications such as monitoring the state-of-health of the composite within the linear elastic regime.

AA16-5 COO Reduction for Semiconductor Parts via ALD Coatings and Recycling of Parts*, **Russell Parise**, I. Iordanov,* QuantumClean, A Business Unit of UCT*; G. Osoro,* Inficon

The semiconductor industry has considerable experience with thermal spray protective coatings of parts in the etch and deposition areas to modify surface chemistry, provide corrosion resistance, or provide a barrier layer.These coatings are effective but are generally thick (150 - 200 µm) and may not provide sufficiently low porosity for parts exposed to reactive gases or plasmas.The ALD process creates high purity thin-films that are dense, highly conformal and defect free. Materials such as Al_2O_3 and other metal oxides are resistant to the reactive halogens that part surfaces see during semiconductor processing.

To address these challenges, ALD coatings have been developed to uniformly coat showerheads, pedestals, and other parts with high aspect ratios with 100 – 500 nm thin-films such as Al_2O_3, SiO_2, or other metal oxides.These films protect the part from the reactive halogen radicals and extend green to green time. Besides protecting the parts from reactive gases, the high aspect ratio ALD coatings on chamber components can serve as a diffusion barrier to avoid metal migration from the part itself and reduce conditioning times.

Additionally, parts with these ALD coatings can be recycled. Using Selective Coating Removal, the ALD protective coating is removed with minimum damage to the substrate, including the high aspect ratio features, before the part is prepared for ALD recoating. The loop essentially extends part life almost indefinitely which decreases cost of ownership.

This paper addresses the recent advances in the use of ALD thin films as a functional, protective coating that enhances part performance and reduces process costs.It will also cover the technology to selectively remove the deposition layer and ALD coating without damage to the part.Surface preparation, final cleaning, metrology and analytical testing for validation will also be discussed.

Keywords: ALD, Al_2O_3, corrosion, diffusion barrier, SiO_2, aspect ratio, etch, CVD

AA16-8 Aqueous Degradation and Nanoscale Coatings of Al_2O_3 via Atomic Layer Deposition (ALD) of $BaAl_2O_4$: Eu^{2+}, Dy^{3+} Long Afterglow Phosphors*, **Erkul Karacaoglu**,* Georgia Institute of Technology, USA and Karamanoglu Mehmetbey University, Turkey*; E. Öztürk,* Karamanoglu Mehmetbey University, Turkey*; M. Uyaner,* Necmettin Erbakan University, Turkey*; A. Okyay,* OkyayTechALD Okyay Technnologies, Turkey and Stanford University*; M. Losego,* Georgia Institute of Technology, USA

In this presentation aqueous degradation studies of $BaAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors synthesized from solid-state reaction methods and coated with nanoscale Al_2O_3 protective layers via atomic layer deposition (ALD) will be presented. The uncoated phosphor powders degrade in water within just 30 minutes of immersion. This degradation directly affects the bluish-green phosphorescence (497 nm), creating both blue- and red-shift which are maximized at 429 nm and 687 nm, respectively. Hydration and decomposition of the $BaAl_2O_4$ phase reveals a continuous change in the phase assemblage over 30 days. ALD coatings of ~10 nm Al_2O_3 protects the phosphor from aqueous degradation upon long-term immersion in water. ALD Al_2O_3 coated $BaAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors retain their phosphorescence for at least 7 days of water immersion. Successful encapsulation of $BaAl_2O_4$-based phosphors will make them possible to store in humid environments or use in applications directly requiring aqueous solution.

ALD Applications
Room On Demand - Session AA17
ALD Applications Poster Session

AA17-1 Atomic Layer Deposition of AlN Films With and Without Plasma. Piezoelectric Effect and Magnetoelectric Coupling With Nickel*, **Noureddine Adjeroud**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Aluminum nitride (AlN) thin films have attracted significant attention for optoelectronics, piezoelectrics-based devices as surface-acoustic-wave resonators thanks to its excellent properties such as wide band gap of 6.2 eV, piezoelectricity along c-axis and high phase velocities of acoustic waves. Those applications, however, require the control of the c-axis (002) crystalline orientation of AlN in order to achieve the highest piezoelectric effect and surface acoustic velocity. Many efforts have been devoted to grow (002)-oriented AlN films. For instance, (002) oriented AlN film can be synthesized by pulse laser deposition, chemical vapor deposition, plasma assisted physical vapor deposition and plasma enhanced atomic layer deposition (PEALD). Nevertheless, those techniques require either elevated temperatures of substrate from 300 to 1000 oC and/or long period of plasma treatment during each cycle. In this study by carefully adjusting parameters of PEALD we were able to tailor preferred orientations of AlN thin films from a preferred (100) orientation to the (002) orientation at low substrate temperature from 180°C to 250 oC. In addition, X-ray photoelectric spectrometry surveys confirmed high quality AlN films with low impurities level of 1% of carbon and 6-7% of oxygen, which are comparable to the literatures. The direct piezoelectric coefficient e31,f measurements (4-point bending method, aixACCT), which were rarely reported on AlN films grown by PEALD, revealed a strong correlation between crystallographic orientations and e31,f value of AlN films; i.e. e31,f coefficient of (100) AlN film was almost “zero”, whereas that of (002) preferred orientation film was measured to 0.38 C.m-2. In addition, we synthesized 2-2 magnetoelectric composites by depositing (002) oriented AlN film of 500 nm thickness on nickel foil with an excellent interface coupling by the highly conformal coating of ALD technique. The low temperature growth of AlN films allowed to unconcern in degradation of magnetic properties of the nickel magnetostrictive film.. The resulting magnetoelectric coefficient was about 3.5 V.cm-1.Oe-1 at 46 Hz. Though, AlN film is grown at temperature as low as 250 °C, the properties of the AlN film and its magnetoelastic coupling are utmost promising for energy harvesting and sensing applications on silicon-based as well as flexible-organic-substrate-based micro-electro-mechanic-system (MEMS) devices.

AA17-2 ALD SnO P-Type Thin Film Transistors and the Influence of Post Fabrication Annealing Conditions on Device Performance*, **Benjamin Peek**,* Pegasus Chemicals, UK*; P. Chalker, M. Werner,* The University of Liverpool, UK*; P. Williams,* Pegasus Chemicals, UK*; F. Alkhalil, S. Das,* PragmatIC Semiconductor, UK

Flexible oxide electronics are integral to the proliferation of the Internet-of-Things (IoT). Currently, the state-of-the-art is predominantly based on unipolar n-type devices (NMOS). A complementary (CMOS) logic capability would greatly expand the range of low-cost flexible electronics, because the static power consumption is much lower than in unipolar based technology. Tin monoxide (SnO) is a candidate for p-type thin film transistors (TFTs) that could be matched to existing NMOS technology.Previously, p-type SnO films and TFTs have been fabricated by ALD (Atomic Layer Deposition) using bis(1-dimethylamino-2-methyl-2-propoxy) tin(II) (Sn(dmamp)2) and H2O vapour [1]. This precursor is synthesised, via an intermediate, namely bis(bis(trimethylsilyl)amide) Sn(II), which has also been used to deposit SnO with water [2]. Here we report the use of a precursor from Pegasus Chemicals, to deposit the channel of SnO-based p-type TFTs via ALD. The liquid precursor has been used to conformally deposit SnO thin films at 150°C with water vapour, onto 200mm wafers as shown in Fig. 1. An X-ray diffraction pattern of an SnO film deposited using 4000 ALD cycles is shown in Fig. 2. The dominant diffraction peaks are from the <001> and <002> planes of α-SnO, indicating the growth has a <001> preferred texture.P-type TFTs were fabricated at PragmatIC Semiconductor based on silicon (p++) back-gated structure, as illustrated in Fig. 3, which shows the TFT characteristics of this device. The α-SnO channel of which was deposited in 500 ALD cycles. Before the patterning of SnO, the wafer exhibited a sheet resistance of Rsh 1.6 MΩ/sq . The TFT characteristics were measured: as-fabricated and after annealing in air (200° C, 1 hr), vacuum (190° C, 1 hr), nitrogen (200° C, 1 hr) and forming gas (350° C, 30 mins). Air annealing (blue) has little effect on the as-fabricated TFTs (black). The vacuum anneal (red) and nitrogen anneal (green) show a similar effect on the device performance, resulting in a marginal decrease in the on and off-current. Forming gas (H2/N2) annealing (FGA) leads to an enhanced on/off ratio, in addition to a negative shift in Von towards 0 V. Potential mechanisms responsible for the effect of different annealing processes on the TFT characteristics will be discussed .The work demonstrates the feasibility of using ALD-deposited tin monoxide to fabricate p-type TFTs at temperatures compatible with flexible oxide electronics manufacturing processes.[1] Jeong Hwan Han et. al, Chem. Mater. 2014, 26, 6088−6091. [2] Jere Tupalaa et. al. Journal of Vacuum Science & Technology 2017, A35, 041506.

AA17-3 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Indium Oxide*, **Ali Mahmoodinezhad**, C. Morales,* Brandenburg University of Technology Cottbus–Senftenberg, Germany*; F. Naumann, P. Plate, R. Meyer,* SENTECH Instruments GmbH, Germany*; C. Janowitz, K. Henkel, M. Kot, J. Flege,* Brandenburg University of Technology Cottbus–Senftenberg, Germany

Indium oxide (In_xO_y) thin films were successfully grown by plasma-enhanced atomic layer deposition (PEALD) using trimethylindium (TMIn) and oxygen plasma (O_2) at low temperatures of 80 to 200 °C. The films were investigated by spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and electrical measurements. The in-situ SE data confirmed a self-saturated growth mechanism with a growth rate of 0.56 Å per cycle within the ALD window (100 to 150 °C) resulting in a well-defined film thickness with an excellent homogeneity of ≥ 98.8% across 4 inch substrates. We found that the refractive index of the layers increases from 2.04 at 80 °C to 2.07 at 150 °C, and it abruptly decreased to 2.02 at 200 °C. Besides, the In_xO_y layers show indirect and direct transitions in the optical band gap with values of 2.8 ± 0.1 eV and 3.3 ± 0.2 eV, respectively. According to XPS, the PEALD-In_xO_y thin films are free of carbon below the surface; also, they exhibit a temperature-dependent indium-rich off-stoichiometry that increases with temperature. Correspondingly, at temperatures ≥ 150 °C, the electrical conductivity of the layers is higher. In addition, a detailed XPS analysis revealed the presence of hydroxyl groups and defect states whose concentrations decrease with rising deposition temperature. Based on the obtained results, we deem our indium oxide thin films to be suitable for high-performance optoelectronic and photovoltaic devices.

AA17-4 High-Reliable Atomic Layer Deposited N-doped GeSe and Its Leaky-Integrate-and-Fire Neuron Application*, **Woohyun Kim**, M. Ha, C. Yoo, J. Jeon, W. Choi, B. Park, G. Kim, K. Woo, J. Kim, Y. Jang, E. Park,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

This study presents the atomic layer deposition (ALD) of N-doped GeSe and its neuromorphic application for leaky-integrate-and-fire (LIF) neuron. The ALD process utilized $Ge^{II}N(CH_3)_2[(N^iPr)_2CN(CH_3)_2]$ and $[(CH_3)_3Si]_2Se$ with an NH_3 co-reagent as Ge- and Se-precursors, respectively. The N-doped GeSe was not deposited by the conventional ALD sequence (Ge-precursor pulse – purge – Se-precursor pulse – purge) without the NH_3 gas. The NH_3 gas changes the surface terminated with $[(N^iPr)_2CN(CH_3)_2]$ to NH_2 group for facilitating ligand exchange reaction with $[(CH_3)_3Si]_2Se$.

The $Ge^{II}N(CH_3)_2[(N^iPr)_2CN(CH_3)_2]$ is stable even at high temperatures (~ 190 ℃) due to the chelating of the ligand, and thus, the ALD window can be extended to high temperatures (Fig. 1(a)). Therefore, this ALD method could be performed at the substrate temperature of 150 ℃, which is significantly higher compared with the previous experiment using $HGeCl_3$ precursor (70 ℃). The ALD process resulted in high-density GeSe thin film deposition with N-incorporation (Fig. 1(b), (c)). In the case of GeSe, the doping of light elements like nitrogen improves amorphous stability, leading to better reliability of Ovonic threshold switching devices. As a result, high crystallization temperature and excellent cycling endurance of GeSe were achieved due to the N-doping effect and high-density thin films by adopting the high deposition temperature (Fig. 1(d)).

Furthermore, the GeSe-based LIF neuron's behavior is verified by the measurement of the electrical waveform using a pulse generator (Fig. 2), and the detailed analysis will be discussed in the presentation.

AA17-5 Zero Temperature Coefficient of Resistance in Back-End-of-the-Line - Compatible Titanium-Aluminum Nitride Nanolaminates Grown by Plasma Enhanced Atomic Layer Deposition, *I. Krylov,* Tower Semiconductor Ltd., Israel*; Y. Qi,* ***Valentina Korchnoy****, K. Weinfeld, M. Eizenberg, E. Yalon,* Technion–Israel Institute of Technology, Israel

Thin film resistors with near-zero temperature coefficient of resistance (TCR) are key passive elements in analog integrated circuits. We report here that near-zero TCR resistors can be obtained by atomic layer deposition (ALD) of TiN-AlN nano-laminates at back-end-of-the-line (BEOL)-compatible deposition temperatures.The ALD method provides an ultimate control of the thickness, composition ratio, coverage and uniformity. The nitride films were deposited using plasma enhanced ALD (PEALD) at 300°C. TDMAT and TDMAA were the metalorganic precursors for deposition of TiN and AlN components, respectively. The properties of the binary TiN and AlN compounds were investigated separately as well to find the temperature window for the ternary PEALD process (FIG. 1). A mixture of ammonia and argon gases was used for reactive plasma. The films were deposited on SiO_2/Si substrates with thermal oxide thicknesses of 3nm and 100nm. The electrical resistivity of the deposited films was measured by the transfer length method (TLM). We patterned and etched the nitride films into resistor channels with a fixed width (120µm) and varying lengths (between 440 and 1310µm) in a TLM structure. The TCR was obtained by measuring the resistivity with varying stage temperatures in the range of -40°– 100°C. The electrical resistivity of the nanolaminate increases and the TCR changes from positive to negative as the AlN content is increased from 0 to 44%, with zero TCR (and resistivity ~450 µΩ·cm) around ~20% (FIG. 2). Microstructure analysis shows that the $Ti_xAl_{1-x}N$ films most likely consist of metallic TiN crystallites embedded in the semiconducting $Ti_yAl_{1-y}N$ amorphous matrix (Fig. 3). Near-zero TCR value of these films is achieved by a superposition of the conduction mechanism inside the conductive TiN crystallites and charge transfer between them through the insulating/semiconducting $Ti_yAl_{1-y}N$ matrix. Both resistivity and TCR in our laminate nitride films were found to be stable for thermal treatment of 500°C/1 h. An insignificant increase in these properties after the post-deposition annealing can be attributed to surface oxidation of the uncapped films. The zero TCR behavior of our nitride films can be achieved in as-deposited films, making them compatible with BEOL process of microelectronic fabrication (350°C – 450°C/1 h), unlike present zero-TCR technology (SiCr-based), which requires annealing at temperature ~550°C. These results pave the way toward BEOL-compatible near-zero TCR thin film resistors, which can significantly reduce capacitance and minimize design complexity of passive analog IC components.

AA17-6 Influence of H_2S Dosage on Surface Roughness of Zn(O,S) Films by Atomic Layer Deposition (ALD), ***Narmatha Koothan****, T. Chou, Y. Yu, W. Cho, J. Su, C. Kei,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Zn(O,S) is a material commonly used as n-type buffer layer in solar cells such as CIGS, CZTS to replace toxic CdS. The optical bandgap of Zn(O,S) can be varied by adjusting the ratio of oxygen to sulfur ratio. The optical and electrical properties of the buffer layer is a crucial factor in photovoltaic devices. Optimization of the optical properties leads to the increase of light absorption in low wavelength region. Beside the optical bandgap, surface roughness, another important property, is essential in solar cell applications. The high surface roughness of the film influences the absorber/buffer layer interface and also increases the reflectance of device. Therefore, we analyzed the influence of H_2S dosage on the surface roughness of Zn(O,S) films. ALD is adapted to deposit the ZnOS films because of its precise control of thickness and composition. In this study, Zn(O,S) film with the ratio of m: n (ZnO: ZnS) 11:1 were grown by ALD. ZnO was deposited with the ALD sequence of 0.2 s of Diethyl Zinc (DEZ), 0.1 s of H_2O separated by 30 s of N_2 purge. ZnS was deposited with the ALD sequence of 0.2 s of Diethyl Zinc (DEZ), 0.1 s of H_2S separated by 30 s of N_2 purge. The schematic diagram of Zn(O,S) deposition is shown in Fig.1. To study the influence of H_2S dosage on the surface roughness, ZnOS 11:1 ratio films with the H_2S dosage of 0.1, 0.3, 0.5 & 1 s were prepared by ALD. The elemental composition of these materials were analyzed by X-ray electron spectroscopy (XPS), shown in Table 1. Fig.2 shows the increased Surface roughness of Zn(O,S) with the increase in H_2S dosage, measured by Atomic force microscope (AFM) . The changes in transmittance and reflectance with the changes in surface roughness, were studied by UV-vis spectrophotometer.

AA17-7 Bias-Enhanced Atomic Layer Annealing for the Deposition of High-Quality Aluminum Nitride Films on Silicon, ***Aaron McLeod****, S. Ueda,* University of California at San Diego*; D. Alvarez,* RASIRC*; A. Kummel,* University of California at San Diego

High-quality AlN films are promising for use as buffer layers for the growth of GaN and InGaN on Si and SiC for use in RF and micro-LED devices. Known deposition methods include metal organic chemical vapor deposition (MOCVD) and sputtering, which both present integration concerns: MOCVD requires high (>700°C) temperature while reactive sputtering yields strained, randomly oriented films.[1-2]

Bias-enhanced atomic layer annealing (ALA) allows for lower temperature deposition of crystalline materials by adding ion bombardment to the end of each atomic layer deposition (ALD) cycle. The substrate is mounted on a negatively biased stage heater and ions are accelerated from the plasma source towards the growth surface.[3] This bombardment enhances surface adatom mobility, leading to the deposition of crystalline films.

Tris(dimethylamido)aluminum (III) and anhydrous hydrazine (N_2H_4) (Rasirc) are used as precursors, while Ne, Ar, or Kr plasma was used for the 20s ion bombardment. For all samples, 500 cycles of ALA AlN (~40 nm) was deposited on HF-cleaned Si (111) substrates at 400 ˚C using -10V, -25V, and -40V bias for each plasma gas. In-vacuo x-ray photoelectron spectroscopy (XPS) and ex-situ grazing-incidence x-ray diffraction (GIXRD) and x-ray reflectivity (XRR) were used to determine chemical and structural composition of the films.

As seen in the GIXRD and XRR data in Fig. 1, all conditions yielded preferential AlN (002) orientation and density within 3% of bulk AlN. The full width at half max of the AlN (002) diffraction peak decreases with increasing ion momentum, indicating the growth of larger crystallites. Chemical composition data from XPS (not shown) indicate stoichiometric AlN with low impurity content of 1.2-4.9 At. % and 1.3-2.5 At. % for C and O, respectively.

Using the Ar -25V ALA condition, 20nm films were deposited to template further AlN growth by reactive sputtering. The GIXRD results of this study, as well as reference films of only sputtered material are shown in Fig. 2. It is observed that the ALA layer successfully suppresses the growth of AlN (103) and promotes (002) oriented growth. In summary, it was found that the crystallinity of the ALA AlN films could be tuned by controlling ion momentum and that these films successfully template sputtered AlN. The strong preferential orientation seen in these studies will allow these films to more effectively be used as templating layers for further GaN or InGaN growth.

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AA17-8 Atomic Layer Deposition of Nio for the Modification of Electro-Catalysts for Alkaline Water Splitting, ***Muhammad Hamid Raza****,* Humboldt-Universität zu Berlin, Germany*; M. Frisch, R. Kraehnert,* Technische Universität Berlin, Germany*; N. Pinna,* Humboldt-Universität zu Berlin, Germany

Different catalytically active oxides are being used as electrode materials for electro-chemical water splitting under alkaline conditions. The catalytic performance of those materials strongly depends on surface composition and morphology. Modifying the surface of such electrodes to increase the number of potentially active sites offers the opportunity to increase the electrode's catalytic efficiency.

We report the synthesis of NiO modified oxides via ALD directly onto the high-surface area electrodes. The developed ALD process for NiO relies on the use of Bis(cyclopentadienyl)nickel(II) and ozone in a thermal ALD process. The composition, morphology, and crystallinity of the deposited film were controlled by varying different deposition parameters. The varying amount, size, and morphologyof the metal oxide catalysts were homogeneously deposited onto a series of metal oxides. The structural and morphological properties as well as the performance and stability in the electrocatalytic oxygen evolution reaction in alkaline media were investigated in a 3-electrode rotating disc setup in order to elucidate performance-controlling parameters.

AA17-11 Plasma-Resistant Mixed Metal Oxide Films

Vasil Vorsa, A. Pavel, Greene Tweed & Co.

To prevent contamination of microelectronic devices during semiconductor processing, chamber components of semiconductor tools are often coated with high purity ceramic coatings such as alumina or yttria that exhibit high resistance to plasma erosion in halogen environments.However, even these materials exhibit erosion over time leading to lower yield and costly down time, especially as the industry moves to smaller node sizes.

To overcome these limitations, there has recently been a major effort (Refs) to find new coating materials and processes leading to improved plasma erosion resistance. There are now emerging plasma-resistant coatings deposited by atomic layer deposition (ALD). Advantages of ALD include conformal, dense, and pinhole-free film that can coat complex 3D shapes and high-aspect ratio holes.

In this work, a number of single component and multi-component metal oxide films (homogeneous and nanolaminate) were evaluated for plasma etch resistance.While normal ALD pulsing schemes were employed to deposit single component Al2O3, SiO2, Y2O3, ZrO2 films, YAlO, YSiO, and YZrO films were deposited by various pulsing schemes including sub and super cycles normally used to deposit nanolaminate films and pulsing schemes to simulate codeposition.The films were then subjected to plasma etching in a fluorine-argon environment utilizing a capacitively-coupled parallel plate plasma reactor.Plasma resistance of each film was assessed through calculating etch rates as measured by thickness changes using ellipsometry and fluorine penetration by XPS depth profiling.

AA17-14 Super-Cycle Atomic Layer Deposition of Indium Gallium Zinc Oxide

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Indium gallium zinc oxide (IGZO) is a promising candidate as a transparent conductive oxide (TCO). The amorphous phase of this compound shows a band gap of 3.0 eV and exhibits a high charge carrier mobility and concentration with reported values of 50-80 cm^2/Vs and 10^{17}-10^{20} cm^{-3}, respectively.[1,2] Therefore, it is well suited for photovoltaic applications, light emitting diodes, and thin film transistors. In contrast to single crystalline TCO's, it is much easier and cheaper to realize IGZO films. To date, the established deposition methods for IGZO layers such as DC/magnetron sputtering and pulsed laser deposition fail when the deposition of uniform films over a large substrate area is required. Also, controlling the elemental composition of the quaternary system is crucial for achieving the desired electrical properties. Atomic layer deposition (ALD) can meet both challenges by combining the ALD cycles of their respective binary compounds in a distinct sequence and ratio. This so-called super-cycle process allows controlling the composition of the target film by adjusting the individual cycle ratio.

In this work, we present a approach to deposit IGZO films by ALD. The depositions have been carried out in a SENTECH plasma-enhanced ALD (PEALD) reactor, in which we applied a thermal process for zinc oxide (ZnO) as well as plasma-enhanced processes for gallium and indium oxide (Ga_2O_3, In_2O_3). The growth mechanism of each individual process within the super-cycle has been investigated and monitored by *in-situ* ellipsometry (i-SE, SENTECH ALD Real-Time-Monitor). An *ex-situ* analysis of the compound has been performed by X-ray photoelectron spectroscopy (XPS) to determine the film composition and correlate it to the expected values based on the super-cycle sequence.

The i-SE revealed a nucleation delay for the thermal ZnO process, making it challenging to properly adjust the cycle ratio. Thus, the thermal ZnO cycle has been replaced by a plasma-enhanced ZnO process, which shows no nucleation delay. In further *in-situ* investigations a higher growth rate for the PEALD-ZnO deposition on a Ga_2O_3 surface than on an In_2O_3 surface was observed. Based on this knowledge, we were able to set-up the ideal cycle sequence for the IGZO process. Accordingly, XPS revealed a direct correlation between the applied cycle ratio and the elemental composition of the film. Together, these findings confirm that a full PEALD super-cycle process is an effective approach to deposit well-defined IGZO films.

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AA17-17 Effect of Precursor on Deposition Behavior of ZrO_2 Atomic Layer Deposition

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Abstract

As design rule of semiconductor device decrease continuously, a wide variety of high-k materials have been evaluated including ZrO_2, HfO_2, TiO_2, and $SrTiO_3$. Among of them, ZrO_2 is the most commonly used dielectric material in Dynamic Random Access Memory (DRAM) capacitor [1-3]. However, Atomic Layer Deposition (ALD) of transition metal materials such as ZrO_2 doesn't show an ideal behavior and the fundamental understanding about correlation of precursor and deposition is needed to develop ZrO_2 ALD process having high quality [4].

In this study, we have investigated deposition behavior of ZrO_2 ALD using [Tetrakis(EthylMethylAmino)Zirconium] (TEMAZ) and [Cyclopentadienyl(Tris(DiMethylAmino))Zirconium] (CTDMAZ) precursors. TEMAZ and CTDMAZ showed different deposition rates and maximum deposition temperature within ALD window, which were related to the thermal stability of Zr precursors. The thermal stability of precursors was related to the effective atomic number (EAN) around the central metal and showed higher value in case of higher electron configuration. Zr atoms of TEMAZ and CTDMAZ have 8e and 12e configuration, respectively. Consequently, CTDMAZ showed 30°C higher thermal stability and 20°C higher ALD maximum temperature than those of TEMAZ.

In the electrical characteristics of the $TiN/ZrO_2/TiN$ capacitor, the dielectric constant and leakage current density were improved when the ZrO_2 film using CTDMAZ was deposited at a high temperature. Analysis of physical properties showed that impurities were reduced and bandgap increased in the ZrO_2 film using CTDMAZ at high temperature.

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AA17-20 Gas-Sensing Properties of Hierarchical Core-Shell Nanofibers: Radial Modulation of Hole-Accumulation Layer

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Semiconducting metal oxide (SMOX) based heterostructured gas sensors have been applied in a wide range of environmental and safety applications. However, structurally well-defined hierarchical core-shell heterostructures are needed in order to illustrate their charge transfer and gas sensing properties. Herein, one-dimensional hematite nanofibers (NFs) were selected as a robust substrate in order to provide a high surface area to the sensing films. Firstly, hematite NFs were synthesized by electrospinning method. Secondly, in order to produce hierarchical p-MOX/hematite core-shell nanofibers (CSNFs), these NFs were coated with well-controlled p-type SMOX shell layers with varying thicknesses by atomic layer deposition (ALD).

The morphological and structural analysis confirmed a conformal coating of the hematite NFs with SMOX shell layer depicting a hierarchical core-shell like architecture, where the thickness of the shell layer was precisely controlled by varying the number of ALD cycles. The DC electrical resistance analysis showed a significant effect of the shell thickness to the baseline conductance and ultimately the gas-sensing properties of the core-shell heterostructures. In addition, the sensing-response of the proposed sensors were studied towards different concentration of the target analytes such as VOCs, hydrogen, CO, NO2 and NO. The gas-sensing response along with the other properties of the CSNFs were optimised in terms of the thickness of the p-type shell thickness and a plausible sensing and transduction mechanism is proposed.

AA17-23 Developing a Model for Describing the Effect of Dispersion of P-Type Co-Catalyst on Photocatalytic Activity Using ALD Prepared CuO_X/TiO_2 Photocatalyst

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Atomic layer deposition (ALD) offers promising solutions for synthesizing well-defined advanced functional nanomaterials such as photocatalysts. Among different photocatalytically active materials, TiO_2 shows an excellent potential for large-scale application; however, it suffers from limited activity to UV light. The decoration of TiO_2 with ultra-fine semiconductor particles with a small band-gap can expand its activity by providing excited electrons/holes from the clusters. However, obtaining the optimum amount/size of co-catalyst is a big challenge for maximizing the photo-activity of TiO_2 in a cost-effective way.

The possibility of depositing uniform nanoparticles (NPs) on the support with controlled size, shape, and morphology using ALD provides an excellent opportunity to obtain high activity photocatalysts with well-controlled structure. We deposited copper oxide (CuO_x) NPs on AEROXIDE® P25 titanium dioxide NPs using a fluidized bed ALD reactor at 250°C using Cu(I)(hfac)(TMVS) and water. The ALD synthesized CuO_x/TiO_2 samples were examined using ICP-OES, TEM, and XPS methods, and were employed as photocatalysts for the solar production of H_2.

A combination of different precursor/co-reactant pulse times and the number of ALD cycles resulted in CuO_x/TiO_2 samples with Cu loading in the range of 0.7-4.8 wt.%. The XPS analysis indicated a mixture of Cu^{1+} and Cu^{2+} in samples that the Cu^{2+} content increases by the increase of Cu content. The averageCuO_x size of samples with Cu content up to 3.8 wt% was about 1.6 nm; the higher Cu concentration resulted in larger clusters. The CuO_x/TiO_2 samples showed significant H_2 productivity improvement compared to pure P25, with about ten times higher produced H_2 for the optimum sample (2.3 wt.% Cu). The higher Cu loading resulted in activity loss.

The evaluation of the H_2 productivity of these samples allowed us to develop a model to describe the activity of CuO_x/TiO_2 photocatalyst as a function of CuO_x loading via predicting the increased photocatalytically active perimeter of Cu_xO clusters; this perimeter is characterized by a higher activity compared to a bare photocatalyst as a result of the injection of photo-excited electrons to the support from co-catalyst. The model results fit well with the experimental data. The XPS spectra of samples showed Ti^{4+} reduction to Ti^{3+} after Cu ALD, with linear increase and plateauing of Ti^{3+} at Cu content of about 2.3 wt.%. Such behavior is predicted precisely by the developed model. This model enables us to predict the optimum CuO_x loading of the CuO_x/TiO_2 system for different particle sizes. This model can be employed for other p-type semiconductor materials as well.

AA17-26 Low-Temperature Deposition of Highly Conformal TiN Films on Pt/C Nanoparticles via Plasma-Enhanced Ald for Fuel Cell Applications

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In this work, we present our efforts on the growth of highly conformal titanium nitride (TiN) films on nano-powders via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). The goal is to deposit a thin protective TiN layer on a Pt/C catalyst for proton exchange fuel cell application in order to prevent carbon corrosion during operation. TiN films were deposited on Pt/C nano-particles (bare and Oleylamine coated) using tetrakis(dimethylamino)titanim(IV) (TDMAT) and Ar/N_2 plasma as the metal precursor and nitrogen co-reactant, respectively. Oleylamine is used to selectively coat Pt catalyst particles and prevent TiN film from formation on them, while carbon is being coated. ALD growth experiments have been performed at 150 °C process temperature. Nano-powders were placed inside a custom-made agitator mechanism to ensure conformal film growth around the particles. Additionally, Si(100) substrate was included in the reactor to serve as a reference sample. Each unit ALD-cycle consisted of 100 msec TDMAT pulse, 10/10 sec purge, and 10 sec plasma exposure at 50 W using Ar/N_2 (50/50 sccm) plasma chemistry. *Ex-situ* multi-wavelength ellipsometry measurements revealed the TiN film growth-per-cycle (GPC) on Si(100) sample at ~0.94 Å/cycle. Bright field Transmission Electron Microscopy (TEM) and High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) were employed to confirm conformal growth of the TiN film on the nanoparticles at the atomic-scale resolution. Additionally, Energy Dispersive Spectroscopy (EDS) mapping was performed to understand the elemental composition of the TiN coated Pt/C nano-powders. The TEM micrographs combined with the elemental EDS analysis demonstrated that homogenous TiN film is formed on Pt/C nanoparticles, having an average thickness of ~5 nm.

AA17-29 Low Temperature Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Films Deposited by Thermal Atomic Layer Deposition Using High Purity H_2O_2

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To implement HZO films to three-dimensional structures and back end of line applications, utilizing atomic layer deposition (ALD) technique, low thermal budget and high conformality are necessary. One of the most well-known ways to reduce the process temperature is to use oxygen plasma as oxygen source [1], However, because of the anisotropic nature of plasma-enhanced ALD with oxygen plasma, using thermal ALD (tALD) is preferable in the aspect of achieving conformal deposition on three-dimensional structures.

In this study, we have demonstrated ALD of HZO films using high purity H_2O_2 in comparison with O_3/O_2 mixture (340 g/m^3) as oxidants. Metal-ferroelectric-metal (MFM) capacitors were fabricated on thermally grown 300 nm SiO_2 layer. 90 nm TiN top and bottom electrode deposited by reactive sputtering and 10 nm HZO with Hf:Zr ratio of 1:1 was deposited between the electrodes using tALD with TDMA-Hf, TDMA-Zr, O_3, and H_2O_2 at 250 °C. The MFM stack then annealed for 60 s under N_2 atmosphere varying 300 °C to 400 °C using rapid thermal annealing (RTA) and patterned to form Au/Pd hard mask to define the area of MFM capacitors. With H_2O_2, higher growth per cycle (GPC) of 0.24 nm/cycle compared to 0.19 nm/cycle for O_3 was observed. Interestingly, even with high GPC HZO films, x-ray reflectometry results showed that with H_2O_2, the HZO film was denser (8.5 g/cm^3) than using O_3 (8.2 g/cm^3). After 400 °C RTA annealing, both HZO samples experienced orthorhombic phase growth with suppressed monoclinic phase growth was observed by X-ray diffraction. Polarization-electric field hysteresis curves and pulse write/read measurement were performed after 10^5 wake-up cycles at 2.5 MV/cm field. HZO samples using H_2O_2 showed higher remnant polarization ($2P_r$) of 62 μC/cm^2 and O_3 showed $2P_r$ of 54 μC/cm^2. Moreover, the HZO samples using H_2O_2 started to exhibit ferroelectric properties from 325 °C, but this was not observable in the case of O_3 at the same temperature, which implies the capability of H_2O_2 for low-temperature applications. Also, HZO using H_2O_2 had lower leakage current and better endurance compared to O_3 samples, and both showed similar breakdown behaviors at 3 MV/cm. Low carbon content (<1 at%) in both samples confirmed by X-ray photoelectron spectroscopy supports this result and shows the capability of carbon removal in both oxidants.

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AA17-32 Effect of NH_3 Flow on Electrical and Mechanical Properties of ALD TiN Thin Films

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In recent nano-scale device applications, especially in DRAM capacitor electrodes, ALD TiN films have been used due to the excellent physical and electrical properties. However, it is necessary to improve mechanical properties such as hardness and modulus, especially under 30 nm film thickness, because ALD TiN films can be easily bent and/or broken during the following integration steps. From the perspective of the intrinsic ALD TiN film property improvement, many studies have been conducted on the ALD TiN thin-film physical and electrical properties, however, there are not many reports focused on mechanical properties such as hardness and modulus. In this paper, we report on the strong relationship between ALD TiN thin-film mechanical and electrical properties and NH_3 flow rate, especially on thinner films from 25 nm to 150 nm.

AA17-35 ALD Al_2O_3 and MoS_2 Coated TiO_2 Nanotube Layers as Anodes for Lithium Ion Batteries

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The miniaturization of Lithium ion batteries (LIBs) as a power source to drive small devices such as smartcards, medical implants, sensors, radio-frequency identification tags etc. has been continuously developed to meet the market requirements of portable applications.[1] In this direction, 3D microbatteries have been considered to satisfy the requirements of these portable devices. Anodic TiO_2 nanotube layers (TNTs) have been recently explored as anodes for LIBs due to their high surface area, low volume expansion, short diffusion lengths for Li⁺ ion transport and good capacity retention even at faster kinetics.[2,3]

Recently, various coatings produced by Atomic Layer Deposition (ALD) on electrode materials have been explored extensively in LIBs. For example, Al_2O_3 and TiO_2 coatings act as a protective layer for the suppression of the solid electrolyte interphase (SEI) in various electrode materials.[4,5] But their influence on increasing the electronic conductivity of the electrode material has not been explored in details. In addition, it is also possible to synthesize using ALD the main electrode materials, such as oxides[6] and sulphides.[7] However, high surfacearea and sufficiently conducting support would be beneficial for these ALD derived materials to support an excellent performance of the batteries. The door for various one-dimensional nanomaterials, such as TNTs, is therefore open

In this presentation, we will show ALD synthesis of Al_2O_3[8] and MoS_2[9] and their combination[10] on TNTs as new electrode material for lithium-ion batteries. We show an influence of different coating thicknesses on the battery performance, in particular on the charging and discharging capacity.

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AA17-38 Experimental Ru Precursors for Cutting Edge ALD & CVD Processes*, **Ivan Zyulkov**,* Umicore, Belgium*; W. Schorn,* Umicore, Germany*; S. Tymek, J. Bachmann,* University of Erlangen-Nuremberg, Germany*; S. Armini, G. Pourtois,* IMEC, Belgium

Integrated circuits downscaling constantly enforces stringent requirements on various properties of functional and sacrificial materials in a device stack, which leads to multiple challenges in process development. Process engineers are working on solutions to pattern alignment and placement error issues, on improvement of etch processes selectivity and line edge roughness, on selective deposition of functional layers and sacrificial hard-mask materials, on ultra-thin layer closure and many others. In addition to the downscaling trend, a general transition to new 3D device architectures is happening in both logic and memory. To deliver deposition processes in compliance with all the requirements mentioned above, ALD and CVD technologies start to play a much more significant role in the process development toolbox than ever before. And new metal precursors with superior volatility and preferential surface reactivity are needed to make cutting edge ALD and CVD processes possible. These new tailor-made precursors enable wider process parameter space, lower chemical consumption and higher process efficiency in comparison with standard on-shelf precursors.

One of the materials expected to be introduced into HVM within the next couple of years is Ruthenium (Ru). Ru is commonly exploited as a liner for copper electroplating and electroless copper deposition. It has a relatively low bulk resistivity (7.1 µΩ cm), a conductive oxide and a high work function (> 4.7 eV). While the demand of Ru precursors for advanced vapor deposition processes is increasing, concerns arise regarding the stability and sustainability of their supply. Industry demands a robust and undisturbed supply chain while the availability of Ru metal on the market is limited, essentially as Ru appears as side product in platinum metal mining and is required in a few industrial applications only. As a major supplier of platinum group metals, Umicore has access to Ru from recycling and metal refining activities and will be a major contributor to provide availability.

In this work we report the development of a Ru ALD precursor from ideation phase, through material supply chain set up and precursor synthesis all the way to thin film property evaluation. We target several Ru applications in IC manufacturing, such as BEOL bottom-up via prefill, conformal Cu liner deposition and area-selective hard-mask deposition for self-aligned block application. We will present our methodology, precursor chemical characterization data and Ru layer properties, such as chemical composition measured by XPS and substrate-dependent selectivity measured by SE and RBS.

AA17-41 Characterization of Al Doped SnO_2 Thin Films With Various Doping Positions Using Atomic Layer Deposition*, **Hyunwoo Park**, N. Lee, Y. Choi, S. Song, J. Lee, G. Lee, E. Lee, S. Lee, H. Jeon, C. Jung,* Hanyang University, Korea

Oxide semiconductors have begun to be used in thin film transistors (TFTs) as a channel layer. Oxide semiconductors are used for a variety of applications due to their advantages such as wide band gap and low process temperature. However, since indium (In) is a rare element that is not abundant on earth, there are problems associated with mass production. Tin (Sn) is an element adjacent to indium on the periodic table, and both Sn^{4+} and In^{3+} have an electron structure of [Kr] $4d^{10}5s^0$, which has a good influence on the electrical characteristics due to the superposition of states of the large s orbital. Tin oxide (SnO_2) has many advantages for applications to thin film transistors such as high transmittance, wide bandgap, and high conductivity.However, the high conductivity tends to reduce the on/off current ratio of TFTs. Therefore, there is a need for a doping method that can reduce the conductivity. In this respect, it has been reported that aluminum (Al) atoms act as suppressors to decrease the conductivity of SnO_2 films. Among the gas phase depositions, atomic layer deposition (ALD) has benefits such as excellent step coverage, uniformity, and thickness control. Also, ALD involves injecting an appropriate amount of dopant into thin films using a cyclic system while controlling the chemical quantities. Another important advantage of ALD is that the dopant can be inserted into the ALD cycle in any order, which makes it very easy to control the position of the dopant. Therefore, it is possible to study the characteristics of thin film transistor achieved by adjusting the doping position of the thin film channel through the ALD process.

In this work, we investigated characterization of SnO_2 thin films with a single Al_2O_3 cycle at various positions using ALD. SnO_2 thin films were deposited with TDMASn, TMA and ozone as a Sn, Al and oxygen sources, respectively. The Al doping positions are investigated using secondary ion mass spectroscopy (SIMS) in 20 nm thickness of SnO_2 thin films. The crystallinity and thickness were analyzed by transmission electron microscope (TEM). The single Al_2O_3 cycle is not affected to crystallinity of SnO_2. Also, on/off current ratio of thin films transistor are changed according to Al doping position using semiconductor analyzer (Agilent B1500A). We also characterize the bonding states and carrier concentration of SnO_2 thin films by analyzing X-ray photoelectron spectroscopy (XPS), and Hall effect measurement. We will present more results in the meeting and will discuss SnO_2 application areas.

ALD Applications
Room On Demand - Session AA2
Energy: Solar Energy Materials

AA2-1 Synthesis of a Composite Dielectric With Conformal Coating of Aluminium Nitiride Over the Distribution of Titanium Nitride Nanoparticles, for Concentrated Solar Power Applications*, **Nikhar Khanna**, M. El Hachemi,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Solar-thermal energy conversion is a promising technology that enables efficient energy harvesting from concentrated solar power (CSP). Recently, there is a lot of interest in metal -insulator based metamaterial absorbers due to complete hold on the permittivity and permeability of these absorbers. In our case the metamaterial absorber would consist of near homogeneous distribution of nanoparticles (Titanium Nitride) in a matrix of (Aluminium Nitride) to form a composite, and an omega shape resonator to couple the electric and magnetic field component of the incoming electromagnetic wave.

Electromagnetic wave absorbers have been investigated for many years with the aim of achieving high absorbance and tunability of both the absorption wavelength and the operation mode by geometrical control, small and thin absorber volume, and simple fabrication.

The present work involves the synthesis of a composite dielectric of approximately 1 µm thickness where nanostructure control is a very challenging task. In this work, we choose a bottom-up approach by constructing a stack of, TiN nanoparticles distribution over a substrate and then a layer of Aluminium Nitride of (85-90nm) thickness, and so on. Titanium nitride particles laid on Si wafer by wet chemical method are coated with conformal coating of Aluminium Nitride, via Plasma- enhanced

Atomic Layer deposition. These components together form the dielectric, which helps in transporting the generated heat in the solar absorber. The control of the morphology at the nanoscale is primordial to improve the material's optical performance, thus in our case maximise the wave extinction inside the composite for the application as solar absorber. The optical properties of the dielectric are measured by ellipsometry and UV-Visible measurements.

In order to choose a composite that is best suited for our requirement, two types of composites were prepared. One with Titanium Nitride powder with particles in the range 20-30 nm with a layer of Aluminium Nitride on top of it, and the other with Titanium Nitride dispersions also with particles in the range 20-30nm with a layer of AlN on top. In both the cases, fewer clusters of 500nm to1um of TiN were present however, enough steps were taken to minimize these clusters into smaller particles.

In conclusion, the work presented here is the comparison of the two kinds of composites with their optical properties (n, k) measured by ellipsometer, and (absorbance, reflectance) measured by UV-Visible Spectroscopy.

AA2-2 *Interface Chemistry in Metal Halide Perovskite/ALD Metal Oxide Systems, Andrea E.A. Bracesco*, *C. Burgess, A. Todinova,* Eindhoven University of Technology, Netherlands*; V. Zardetto,* Solliance Solar Research, Eindhoven, Netherlands*; D. Koushik, W. Kessels,* Eindhoven University of Technology, Netherlands*; I. Dogan,* Solliance Solar Research, Eindhoven, Netherlands*; C. Weijtens,* Eindhoven University of Technology, Netherlands*; S. Veenstra, R. Andriessen,* Solliance Solar Research, Eindhoven, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The conversion efficiency of perovskite solar cells, PSCs, has surpassed 25%.[1] The present PSC architecture includes organic charge transport layers, CTLs, which in certain cases limit the long-term stability and device's efficiency. Metal oxide CTLs, such as ALD metal oxides, are deemed valid alternatives. Among them, NiO and SnO_2, always processed prior to the synthesis of the absorber, are adopted as hole, HTL, and electron transport layers, ETL, respectively.[2,3] Instead, ALD processing directly on top of the perovskite is a major challenge yet to be solved. A well-known example is SnO_2: processed directly on perovskite leads to poor cell performance.[4,5,6] Instead, with the inclusion of an organic buffer layer, it leads to highly efficient and stable devices.

In this contribution[7], we systematically investigate the chemical changes occurring at a $CsFAPb(I,Br)_3$ perovskite (sub-)surface upon ALD growth of SnO_2 and TiO_2. TiO_2 is less investigated in literature, but it allows the comparison in terms of reactivity of the perovskite to similar ALD metalorganic precursors, namely tetrakis(dimethylamido)-Sn(IV) (TDMA-Sn) and TDMA-Ti(IV), with H_2O as the co-reactant in both cases.

The bulk crystalline structure of the perovskite absorber is not affected by the ALD growth, as inferred by XRD analysis. Instead, XPS analysis reveals that the growth of SnO_2 is accompanied by the formation of molecular halide species at the perovskite/metal oxide interface. In parallel, the initial growth of SnO_2 is characterized by sub-stoichiometry and sub-gap defects present above its valence band maximum, associated to Sn(II) states, as observed by UPS. We speculate that a redox reaction involving Sn(IV) metal centers of the ALD precursor and halide anions in perovskite occurs, leading to the reported defects. These sub-gap states are expected to reduce the charge selectivity of SnO_2, since they can promote hole injection from the perovskite valence band to that of SnO_2, thus inducing non-radiative electron-hole recombination. The chemical changes and the decreased charge selectivity at the perovskite/SnO_2 interface support the poor performance of devices with SnO_2 grown directly on top of the absorber. As for TiO_2, instead, we observe limited chemical modifications. Devices employing TiO_2 directly grown on perovskite, show a promising (unoptimized) efficiency of 11%.

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AA2-3 ALD of Lead Halide Perovskites*, Jake Vagott*, *K. Bairley, A. Castro Mendez, C. Perini, J. Correa-Baena,* Georgia Institute of Technology

Perovskite solar cells (PSCs) have quickly risen in efficiency since their initial fabrication in 2009, with the current record power conversion efficiency (PCE) being 25.2% [1]. Quickly approaching the Shockley—Queisser limit of 33% for single-junction solar cells, stability and scalability research has become crucial. While solution deposition of the perovskite absorber layer by spin-coating has resulted in the highest efficiency devices so far, vapor deposition methods have shown promise and may help resolve both the stability and scalability problems that PSCs are currently facing. Atomic layer deposition (ALD), as a vapor deposition process, provides advantages such as fine thickness control, improved conformity, high uniformity, and ability to be incorporated into existing industrial processes such as roll-to-roll manufacturing. The stoichiometry of the perovskite may also be easily tuned through manipulation of the precursor doses. My work focuses on depositing perovskite through a two-step ALD/ molecular layer deposition (MLD) hybrid process, with ALD referring to the inorganic aspects of the process and MLD incorporating organic materials. The first step, which we have recently achieved, is to deposit a conformal lead iodide film which may be converted to methylammonium lead triiodide ($MAPbI_3$) through exposure to methylammonium iodide (MAI). For the lead precursor, $Pb(dmamp)_2$ was chosen as it is more volatile than other common lead precursors such as $Pb(acac)_2$ and has not shown signs of CVD—like growth which has been the case with $Pb(tmhd)_2$ [2]. HI (aq) was chosen as the iodine precursor due to its high vapor pressure and reactivity. The precursors involved are easily accessible through commercial means and do not require any additional processing before use. The second step, which we are currently developing, involves the introduction of a third precursor within every cycle of the previous recipe, which would allow for an effective ALD/MLD process for $MAPbI_3$. Once we are able to deposit highly uniform perovskite thin films by ALD/MLD, this will allow us the ability to deposit 2D perovskite passivation layers which will help improve stability by decreasing defects at the perovskite/charge transport layer interface. This will increase moisture and thermal stability in the PSCs while also being a scalable process.

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AA2-4 Atomic Layer Deposition of $Zn_{1-x}Mg_xO$ as Transparent Conducting Films for Chalcopyrite Solar Cells*, Poorani Gnanasambandan,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; M. Sood,* University of Luxembourg*; N. Adjeroud,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; R. Leturcq,* luxembourg Institute of Science and Technology (LIST), Luxembourg*; S. Siebentritt,* University of Luxembourg

We investigate atomic layer deposited zinc magnesium oxide films with varying Mg content as transparent conducting films and as electron transport layers for chalcopyrite solar cells. Previous studies on the impact of $Zn_{1-x}Mg_xO$:Al as transparent electrodes and Mg doped ZnO thin films for the window layer of CIGS $Cu(In,Ga)(S,Se)_2$ solar cells employed co-sputtering, electrodeposition and ALD respectively [1][2][3][4]; these were limited to fixed composition and deposition temperatures. We examine the effect of $Zn_{1-x}Mg_xO$ films, deposited by atomic layer deposition (ALD) under different growth conditions, on the performance of high-bandgap solar cells based on $Cu(In,Ga)S_2$ absorbers.

Optimizing a ternary process by mixing two binary ALD process has its challenges [5]. We achieve high degree of control on composition by optimizing the growth conditions with varying deposition temperatures and supercycle parameters such as pulse ratios and bilayer period. With the advantage of low temperature and highly conformal thin film growth, we study ALD grown $Zn_{1-x}Mg_xO$ with x varying from 0.1 to 0.4 and elucidate the effect of doping on the band alignment, electrical and optical properties. By varying Mg content we were able to achieve 11% efficient $Cu(In,Ga)S_2$ solar cell with an open-circuit voltage of 941 mV.

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ALD Applications
Room On Demand - Session AA3
Energy: Batteries and Energy Storage

AA3-1 Revealing the Control of Lithium Plating Microstructure Derived from ALD-Grown TiO_2*, Solomon Oyakhire,* *W. Huang, Y. Cui, S. Bent,* Stanford University

Lithium (Li) metal batteries are desirable as rechargeable storage devices due to their high energy density; however, their practical implementation is hindered by the difficulty in controlling the Li metal plating microstructure. Artificial solid-electrolyte interphases (SEIs) have shown the potential to curtail the electrochemical instabilities of lithium, and atomic layer deposition (ALD) is commonly employed for the synthesis of thin-film artificial SEIs such as Al_2O_3 and alucone. However, these films quickly become delaminated because of their innate resistance to the cyclic shuttling of Li ions, resulting in marginal improvements in cell performance.

While previous ALD studies have focused on directly coating the top of Li metal with thin-film artificial SEIs, we adopt a different approach, situating the ALD film beneath Li metal and directly on the copper current collector. We show that by depositing TiO_2 directly on the Cu current collector, we can control the deposition morphology of Li in the widely studied ether-based electrolyte - 1M LiTFSI in a 1:1 mixture of 1,3 dioxolane and 1,2 dimethoxyethane, with 1 weight percent $LiNO_3$ as an additive. By optimizing the thickness of TiO_2, we reveal that lithium nucleates into large deposits atop the TiO_2 film under significantly reduced overpotential, resulting in a reduction in contact surface area with the electrolyte and an increase in cell performance. We report substantial improvements in cycling efficiency with an average Coulombic efficiency of 96% after 150 cycles at a current density of 1 mA cm^{-2} in Li/Cu cells. In comparison to the unmodified cells, voltage profiles for the champion TiO_2-modified cell display negligible loss in charge capacity in the mid and late-stage electrochemical cycles, indicating an improvement in the reversibility of lithium stripping and plating.Using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS), we establish that lithium plates atop TiO_2, rather than beneath it, suggesting that the presence of TiO_2 supports the enhanced reversibility of Li stripping and plating. Also, we utilize coulometry and cryogenic transmission electron microscopy (cryo-TEM) measurements to establish that prior to its nucleation, Li reacts with TiO_2 to form an amorphous Li_xTiO_2 complex. We propose that this complex serves as a lithiophilic layer that promotes the coalescence of large lithium particles and improves cell performance.

AA3-2 Li, N co-controlled Lithium Phosphorous Oxy-nitride(LiPON) Coating for Three Dimensional Thin Film Solid-state Batteries (3D TSSBs) using ALD*, Ha Yeon Kwon,* *S. Hong, T. Park,* Hanyang University, Korea

Recently, various types of solid electrolytes have been studied due to the stability problem of liquid electrolytes.[1] At the same time,three-dimensional thin film solid-state batteries for microbatteries is in the spotlight due to reduced device size. LiPON is the most commonly used solid material for implementing 3D TSSB. LiPON is chemically stable by having a wide electrochemical window and can be applied on flexible substrates with amorphous phase. [2], [3] Unfortunately, LiPON does not have high ionic conductivity among all solid electrolytes. To compensate this point, existing studies have conducted studies to increase ion conductivity by controlling the composition of LiPON. Existing studies have noted that ion conductivity increases with increasing N content of LiPON. However, there were several problems in the process of adjusting the N content. [4], [5], [6] In this study, Li, N composition of LiPON was co-controlled by adjusting ALD super cycleof the LiPON and LiN. By simultaneously adjusting Li and N content, the ion conductivity of LiPON is improved. In addition, a very uniform 3D TSSB can be produced by depositing LiPON using ALD. Details of experimental methods and results will be presented.

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AA3-3 Rational Modification of $LiMn_2O_4$ Surfaces by Controlling the Acid-Base Surface Chemistry of Atomic Layer Deposition*, D. Kang,* Argonne National Laboratory, USA*; R. Warburton,* Purdue University, USA*; A. Mane,* Argonne National Laboratory, USA*; J. Greeley,* Purdue University, USA*;* ***Jeffrey Elam,*** Argonne National Laboratory, USA

Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) coatings can suppress undesirable electrochemical reactions between lithium ion battery (LIB) cathode surfaces and the organic liquid electrolyte. However, our limited understanding of ALD cathode coatings restricts our ability to predict which coating/cathode combinations will succeed. In this study, we performed a combined theoretical-experimental study of a model coating/cathode system aimed at elucidating synthesis-structure-property relationships. We selected five ALD Al precursors exhibiting a range of Lewis acid-base properties to establish trends in the ALD Al_2O_3 chemistry on $LiMn_2O_4$. Density functional theory calculations deduced a correlation between the Lewis acidity of the ligands and the ALD thermochemistry. X-ray photoelectron spectroscopy and *in situ* infrared spectroscopy measurements supported these predictions and further revealed how the Al precursors modify the $LiMn_2O_4$ atomic and electronic surface structure. Finally, coin cell electrochemical measurements established the link between materials properties and device performance. We discovered that while the Mn oxidation state is strongly influenced by the Lewis acidity of the precursor ligand, the surface coverage and thickness of the Al_2O_3 coating are a more representative descriptor of the electrochemical performance measured in coin cell experiments.

AA3-6 ALD of Thin-Film Na_xMn_yO Cathode Materials for Sodium Ion Batteries*, Nikhila Paranamana,* *M. Young,* University of Missouri, Columbia

In recent years, sodium ion batteries have been of increasing interest due to the limited availably of lithium resources for the production of lithium-ion batteries. Because of its abundance in the earth's crust and similar chemical properties to lithium, sodium is viewed as an attractive alternative to lithium. Unfortunately, sodium ion batteries suffer from materials instability issues that limit cycling performance. For example, sodium manganese oxide (Na_xMn_yO) is a promising cathode material for sodium ion batteries but suffers from chemical and structural degradation during electrochemical cycling. Unfortunately, it is difficult to understand the origins of Na_xMn_yO degradation because the local behavior at the Na_xMn_yO surface cannot be observed *in situ* within assembled battery cells. In this work aim to enable the study of the degradation processes in Na_xMn_yO by creating model thin film Na_xMn_yO using atomic layer deposition (ALD). We report on the ALD growth Na_xMn_yO using alloys of MnO_x and NaOH ALD chemistries. $Mn(thd)_3$ and O_3 precursor doses are used to form MnO_x, while Na^tOBu and H_2O doses are used to form NaOH. We examine the effect of mixing these ALD chemistries in varying ratios on the growth behavior and final material composition and structure, and characterize the optical and electrochemical properties of the resulting films. In particular we identify that NaOH facilitates nucleation of MnO_x, and identify slow oxidation processes requiring >300 s O-_3 exposures for saturation. Correspondingly, the growth rates of MnO_x using 6 s and 300 s O_3doses were measured to be 0.12 Å/cycle and 0.42 Å/cycle, respectively. The Na_xMn_yO alloy growth proceeds with a linear growth rate of 8.88 Å/supercycle. Additionally, our studies suggest that at high MnO_x content, the NaO^tBu exposure yields a bulk sub-surface reaction with MnO_x. This work expands upon previous work and contributes to growing understanding of the ALD-growth of alkali-containing ternary oxides.

ALD Applications
Room On Demand - Session AA4
Applications in ULSI FEOL: High-k

AA4-1 Plasma Impact on the Hfo_2 High-K Dielectric: Continuous-Wave Plasma Etch Versus Quasi-Atomic Layer Etch*, Dunja Radisic,* *Q. Smets, T. Schram,* IMEC, Belgium

Etch stop layers (ESL) are commonly used to protect critical films. This is also the case for 300 mm 2D material integration where HfO_2 ESL is used first for the contact trench etch, and again for the damascene high-k first/top gate last process steps. For the latter, the HfO_2 ESL also serves as top gate dielectric and is hence highly sensitive to plasma-induced damage (PID).

In this paper, two main approaches were investigated for the SiO_2 removal stopping on HfO_2. Conventional, Continuous-Wave (CW) plasma experiments (Fluorine-based) were performed in the ICP, and the Quasi-Atomic Layer Etch (Q-ALE) in CCP reactor, both from Lam Research Corporation. The goal was to explore Q-ALE and make a general comparison between the two approaches. The advantage of ALE, as well as Q-ALE over CW plasma etch is its unique capability to remove the material with an angstrom precision, causing minimal or no damage and material removal with high etch selectivity.

Simple metal oxide metal capacitor (MIMCAP) test vehicle was used for the study. First, a 10nm TiN bottom electrode was deposited on Silicon wafers, followed by a 10nm HfO_2 layer and a SiO_2 hard mask. The SiO_2 is etched with a spin-on carbon/spin-on glass/photoresist stack, stopping on the underlying HfO_2. Following the plasma processing, the TiN/W top electrode metal stack is deposited in the trenches, and planarized with chemical mechanical polishing (CMP) to electrically isolate the devices.

Our results show that for the CW approach, longer over-etch (OE) thins the HfO_2, and consequently, increases the leakage current and lowers the breakdown voltage. In the case of Q-ALE, the HfO_2 thickness is intact even with the prolonged OE, implying high process selectivity to HfO_2, with no morphological or electrical evidence of PID. However, in the case of Q-ALE, longer OE causes more spread in the electrical performance. This is likely the result of more residues, formed during the passivation step, and remaining on the HfO_2 surface after processing. (Further process performance improvement can be potentially achieved using the effective post-plasma cleaning, but it was not the goal of this study).

We conclude that Q-ALE is a promising technique for the applications where the HfO_2 ESL also serves as the gate oxide. The high etch selectivity and low PID make it ideal for novel integration flows, like 300 mm 2D material integration.

AA4-2 Self-Aligned Atomic Layer Deposited Gate Stacks for Electronic Applications*, **Amy Brummer**, A. Mohabir, M. Filler, E. Vogel,* Georgia Institute of Technology

The formation of self-aligned MOSFET gate stacks via area-selective atomic layer deposition (AS-ALD) of high-κ dielectric and metal films offers a route to reduce the number of lithography steps, maintain a low thermal budget, and improve performance by eliminating overlap capacitance. In this work, a new method for bottom-up masking of semiconductor surfaces and nano/microstructures is combined with AS-ALD to fabricate a high-performance gate stack that is self-aligned to the underlying doped source-drain regions. We begin with the SCALES process, which involves a poly(methyl methacrylate) (PMMA) brush grown from a silicon surface [1]. The PMMA brush is then patterned via a mild selective etching of the underlying semiconductor based on the Si dopant concentration. KOH etches lightly doped Si much faster than heavily doped Si, allowing for selective removal from only the lightly doped regions. The full gate stack is then deposited via AS-ALD in areas where the brush has been removed, as shown in Figure 1. Figure 2 shows XPS data of an example gate stack sequence deposited via AS-ALD, including a HfO_2 dielectric and a Pt gate electrode. Both spectra show good selectivity of deposition toward the regions where PMMA had been removed. Figure 3 shows the C-V characteristics of a gate stack on both a silicon substrate that did not undergo the PMMA process as well as a silicon substrate in which the PMMA was removed via etching. The C-V characteristics are almost identical for both cases indicating that the PMMA brush growth and removal does not strongly impact the silicon-HfO_2 interface. The maximum capacitance was used to determine a relative dielectric constant of ~24 which is expected for HfO_2. The interface state density was extracted from the C-V characteristics to be on the order of 10^{12} cm^{-2}. Ongoing work aims to reduce defect density in this and other high-κ dielectrics (e.g. TiO_2, Al_2O_3, ZrO_2).

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AA4-3 Film Characteristics of Lanthanide Oxide Thin Film by Using Atomic Layer Deposition Method*, **Se-Won Lee**, M. Kim,* Merck Electronics, Korea (Republic of)*; S. Ivanov,* EMD Electronics

Lanthanide oxide films possess a wide variety of functional properties. In particular, using them as insulators in MIM structures offers a number of advantages over silicon dioxide. Lanthanide oxide based thin films can be used as gas sensors or hard mask. They are potentially attractive materials for the fabrication of multi layer optical coatings, beam splitters, passive components of integrated circuits, and heat based laser recording devices. Among them, terbium oxide (Tb_2O_3) and gadolinium oxide (Gd_2O_3) have proven to be promising materials for conventional silicon dioxide replacement in nano device applications. It has a relatively high dielectric constant (14 ~ 20) and a large band gap. Our research examines the electrical and physical characteristics of TbO_x and GdO_x thin film by atomic layer deposition (ALD) with as-dep and post rapid thermal annealing (RTP) to improve dielectric characteristics and optimize performance for potential application in nano devices.

Here, we report thermal ALD of TbO_x and GdO_x thin films using high purity Tris(i-propylcyclopentadienyl) terbium(III) (Tb(iPrCp)3) and Tris(i-propylcyclopentadienyl)gadolinium(III) (Gd(iPrCp)3). Deposition of both films was investigated by thermal ALD process with ozone reactant at 150-350 ^oC on Si and TiN substrates. After film deposition, RTP was conducted to observe post annealing effects. Some ALD conditions, including ALD window, and other film properties were very similar to the two films. In both films, amorphous phase with no XRD peak was observed at 200 ^oC samples, but crystallization peak was observed over 250 ^oC. The film density of GdO_x film was ~ 15% higher than the TbO_x film. XPS results showed that carbon is detected in 200 ^oC samples, but it is not detected at temperatures above that. Both samples showed a good step coverage of more than 90% at 200°C, but step coverage was deteriorated rapidly in samples of more than 250°C. Dielectric constant was measured by TiN/TbO_x or GdO_x/TiN (MIM) structure.

As a result, we conducted atomic layer deposition of lanthanide oxide, TbO_x and GdO_x films and analyzed its properties. Both films showed low process temperatures of 200 ^oC, good step coverage, and high dielectric constant, so these characteristics are expected to be used in applications such as high-k gate insulators or hard mask.

ALD Applications
Room On Demand - Session AA7
Applications in ULSI BEOL: Interconnects, Diffusion Barriers, Low-k

AA7-1 Grain-Resistivity Relationship of Ru ALD Precursors*, **Michael Breeden**, V. Wang,* University of California at San Diego*; R. Kanjolia, M. Moinpour, J. Woodruff,* EMD Performance Materials*; H. Simka,* Samsung*; A. Kummel,* University of California at San Diego

Ru is viewed as an alternative to Cu and Co interconnect layers at M0/M1 due to its lower effective resistivity in confined vias. In addition, Ru's low diffusion into porous low-K dielectrics (SiCOH) removes the need for a barrier layer, further decreasing effective resistivity [1,2]. However, the search for a Ru ALD process that can deposit Ru with near-bulk resistivity (6 μΩ·cm) is ongoing, with an emerging interest in selective ALD without passivants. In this work, the grain structure-resistivity relationship for 300C Ru ALD with precursors Ru-Carish ($Ru(IHD)_2(CO)_2$) and $Ru(CpEt)_2$ using O_2 as co-reactant were investigated by four-point-probe measurements, in-situ X-ray photoelectron spectroscopy (XPS) for chemical composition, and X-ray diffraction/reflectometry (XRD/XRR) for grain size and thickness.

Ru ALD precursor dose studies have shown a relationship between the precursor dose and resistivity. To limit pressure through the turbomolecular pump, multiple precursor pulses were dosed to control dosing. For Ru ALD using Ru-Carish on SiO_2, doubling the Ru-carish dose decreased resistivity from 18.5 to 10.2 μΩ·cm at 40 nm thickness. This effect can be attributed to the additional precursor dose consuming oxygen to form volatile RuO_4 resulting in a film with less oxygen content. Furthermore, film thickness can be scaled to 16 nm without increasing resistivity, consistent with studies showing the deposition mechanism involving the presence of adsorbed oxygen, promoting nucleation and reducing resistivity [3].

While the Ru-Carish process requires passivation for selective ALD, inherent selectivity using $Ru(CpEt)_2$ is demonstrated with low resistivity. Substrate selectivity for the $Ru(CpEt)_2$ precursor on SiO2 was demonstrated, with increased oxygen dose increasing the growth rate, but retaining high selectivity after 350 cycles. A resistivity-oxygen relationship can be observed, with a doubling of oxygen dose reducing resistivity from 14 to 9 µΩ·cm for a 30 nm film and XRD showing an increase in grain size from 18 nm to 28 nm for the Ru(002) orientation. Additionally, post deposition forming gas anneal at 450C for 30 min further reduced the resistivity to 8.1 µΩ·cm. These low resistivity Ru ALD processes have potential to allow for low-resistivity Ru films in barrierless via filling for M0/M1 interconnect fill, and the $Ru(CpEt)_2$ precursor shows promise for selective Ru ALD without passivation.

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AA7-2 Atomic Layer Deposition of RuO_2 Using a New Metalorganic Precursor as a Diffusion Barrier for Ru Interconnect*, **Youn-Hye Kim,*** Yeungnam University, Korea (Republic of)*; Y. Kotsugi,* Tanaka Precious Metals, Japan*; T. Cheon, R. Ramesh, S. Kim,* Yeungnam University, Korea (Republic of)

The extremely narrow dimensions required for the metal interconnect in the sub-10 nm technology node would lead to very high electrical resistance of Cu due to the significant influence mainly from the surface scattering of electrons. For these reasons, the trend in interconnect technology is changing from Cu to Ru due to its low resistivity at narrow line width. However, there are some reports that Ru starts to diffuse into Si at temperature above 700°C. Therefore, a diffusion barrier layer is required to prevent diffusion of Ru that degrades electrical properties. In this regard, RuO_2 has good properties as a diffusion barrier, such as low resistivity(~46 µΩ・cm), high chemical and thermal stability. In this study, the RuO_2 thin films were grown at the relatively low temperature of 180 °C by ALD using the new liquid Ru precursor, tricarbonyl (trimethylenemethane) ruthenium and O_2 molecules for diffusion barrier application of Ru interconnect. For optimization of deposition parameters, the effects of pulsing time ratio (t_{O2}/t_{Ru}) and deposition pressure on the formation of RuO_2 phase were investigated. The formation of a RuO_2 phase is favorable with increasing the pulsing time ratio (t_{O2}/t_{Ru}) and deposition pressure. It was also demonstrated that Ru single phase, the mixture phase of Ru and RuO_2, and RuO_2 single phase could be controllably grown with deposition condition. The ALD-RuO_2 films deposited with optimized conditions have a resistivity of ~103 µΩ・cm and a growth rate of ~0.056 nm/cycle with short incubation cycles of 15. The non-barrier layer structure [ALD-Ru(50 nm)/Si] began to lose its stability by forming ruthenium silicides at 750 °C, while the structure with a barrier layer [ALD-Ru/ALD-RuO_2 (5 nm)/Si] were stable up to 850 °C. This indicates that the ALD-RuO_2 thin films have superior performance in preventing the diffusion of Ru. Furthermore, it is expected to improve the process throughput by depositing in the same chamber using same precursor and reactant as Ru.

Acknowledgements

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ALD Applications
Room On Demand - Session AA8
Memory Applications: DRAM

AA8-1 Influences of Oxygen Source and Substrate Temperature on Growth Mechanism of Atomic Layer Deposited Magnesium Oxide Using Bis(Cyclopentadienyl)Magnesium Precursor*, **Bowen Wang,** J. Choi, H. Kim, S. Hyun, H. Lee, C. Hwang,* Seoul National University, Korea (Republic of)

This research mainly studied the dissimilarities of MgO thin film's growth mechanisms in the atomic layer deposition (ALD) process depending on the oxygen sources, such as O_2 plasma, O_3, and H_2O (Fig. 1a, b). The bis(cyclopentadienyl)magnesium (Cp_2Mg) was adopted as the Mg-precursor. The effects of the oxidizing power and the temperature from 230℃ to 390℃ on the Cp-ring rupture reactions in the ALD process were analyzed by ex-situ techniques, such as X-ray diffraction/reflectometry, X-ray photoelectron spectroscopy (Fig. 1c and d), time of flight secondary ion mass spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy and transmission electron microscopy (Fig. 2a, b). It was intended to examine the crystallization, impurities and their depth profiles, stoichiometric ratio, surface/interface bonding, relative volumetric density. At relatively low substrate temperature (~ 250℃), albeit the similar crystallization and surface morphology were measured by glanced incidence X-ray diffraction and the field emission scanning electron microscope, O_2 plasma-enhanced ALD MgO showed the least impurity level and highest density. At the same time, the O_3-based thermal ALD-MgO exhibited the lowest density and highest impurity level among those three co-reactants. Unlike the overgrowth and void formation (Fig. 2b) at the growth temperature of 290℃, the O_3 ALD showed a comparably lower impurity level than the plasma-enhanced ALD at 335℃. Figure 1e shows the suggested ALD reaction mechanism. This was corroborated by the electrical characteristics using the planar metal-insulator-metal capacitors (metal layer was TiN). Furthermore, the pre-, post-annealing conditions were optimized for the optimal leakage current and dielectric constant of ALD-MgO.

AA8-2 Atomic Layer Deposition of Y-Doped TiO_2 Thin Films to Decrease the Leakage Current for DRAM Capacitor Applications*, **Tae Kyun Kim**, C. Hwang,* Seoul National University, South Korea

This work reports the electrical behavior of Y-doped TiO_2 (YTO) thin film as a dielectric layer for a capacitor of dynamic random access memory. The electrical performance of YTO thin films is comparable to that of Al-doped TiO_2 (ATO) thin films (Fig. 1(a)), which is well-known for its excellent leakage current property among other series of doped rutile TiO_2 thin films [1]. Nonetheless, YTO thin films appear to suppress the leakage current via a different mechanism from that of the ATO thin films. The large ionic size of Y ion compared with the Ti inhibits the efficient diffusion of them into the lattice of the rutile TiO_2 thin film, which results in a nano-laminate structure (Fig. 1b). In contrast, the small ionic size of Al in ATO fluently diffused into the TiO_2 film and form acceptor states. Therefore, it could be guessed that the leakage current suppression mechanism in YTO film is similar to that in the $ZrO_2/Al_2O_3/ZrO_2$ case, where the interrupted columnar grain structure of the ZrO_2 layer has contributed to the leakage current control.

AA8-3 Improved Properties of the Atomic Layer Deposited Ru Electrode for Dynamic Random-Access Memory Capacitor Using Discrete Feeding Method*, **Dae Seon Kwon,*** Seoul National University, Korea*; W. Jeon,* Kyung Hee University, Korea*; D. Kim, T. Kim, H. Seo, J. Lim, C. Hwang,* Seoul National University, Korea

A ruthenium (Ru) thin film as a bottom electrode of dynamic random-access memory (DRAM) capacitor was grown via atomic layer deposition (ALD) with a discrete feeding method (DFM). The DFM-ALD was conducted by dividing the Ru source feeding and purge steps of the conventional ALD process into four steps (shorter feeding + purge times). The DFM-ALD could efficiently eliminate the adverse effects of the Ru precursors' physisorption and byproducts during the ALD process, resulting in a more fluent ALD reaction. The physicochemical properties of the Ru films deposited via conventional ALD, DFM-ALD, and sputtering were investigated and compared in detail. The Ru films deposited via DFM-ALD showed a higher density, smoother surface morphology (Fig.1), and preferred orientation of a (101) phase compared to the conventional ALD process. Also, the Ru films grown via DFM-ALD showed higher susceptibility of oxygen atoms into the Ru films, resulting in a higher proportion of the RuO_2 layer on the Ru film surface, which is formed during the subsequent ALD process of the high-*k* TiO_2 thin film. Such a higher RuO_2 portion led to more fluent lattice-matched local epitaxial growth of the TiO_2 films with a rutile structure as well as the smoother surface morphology without local protrusions. The possible mechanism of the improved TiO_2 film growth mechanism was suggested (Fig. 2). These improvements in the physical performances also improved the electrical properties of the $Pt/TiO_2/Ru$ capacitors. A decrease in the interfacial component of equivalent oxide thickness by ~ 0.1 nm could be achieved by the DFM-ALD process compared with the cases on the sputtered Ru film. Consequently, minimum EOT values of ~0.76 nm and ~0.48 nm were obtained with enough low leakage current density ($<10^{-7}$ A/cm^2 at 0.8 V) for TiO_2 and Al-doped TiO_2 (ATO) dielectric films, respectively. The minimum EOT of 0.48 nm was comparable to the most remarkable results from the ATO/RuO_2 layers, which would have induced integration issues caused by the reduction of RuO_2. This finding indicated that the electrical performance of the high-*k* dielectric film was determined by not only the surface morphology but also the chemical properties of the underlying Ru substrate.

**AA8-6 A Comparative Study on the Crystallization Behavior of Atomic Layer Deposited ZrO_2 / Y_2O_3 / ZrO_2 Dielectric Thin Films for DRAM Capacitors*, Haengha Seo*, *D. Kim, D. Kwon, J. Lim, T. Kim, H. Paik, C. Hwang,* Seoul National University, Korea (Republic of)

ZrO_2 / Al_2O_3 / ZrO_2 (ZAZ) thin films have been applied as a representative dielectric for metal-insulator-metal (MIM) capacitors in mass-produced dynamic random-access memory (DRAM) devices. However, the inserted Al_2O_3 layer required for the leakage current suppression degraded the overall crystallinity of the dielectric film, resulting in a much higher equivalent oxide thickness (EOT) compared with the undoped ZrO_2 film as the films became thinner (< 6 nm).

In this work, ZrO_2 / Y_2O_3 / ZrO_2 (ZYZ) thin films were grown on TiN (bottom) electrode by atomic layer deposition (ALD) using $Zr[N(CH_3)C_2H_5]_4$ and $Y(EtCp)_2(^iPr\text{-amd})$ as precursors. ZAZ films were also deposited in the same manner for comparison. The thicknesses of both the Y_2O_3 and Al_2O_3 layers were fixed at ~ 0.3 nm, and they were deposited on top of the ~ 2.1 nm thick ZrO_2 bottom layer. Only the top ZrO_2 layer thickness was varied between 0 and 8 nm. All samples were subjected to post-metallization annealing (PMA) at 600 °C, after TiN/Pt (top) electrode deposition.

As can be seen from **Figure 1**, the EOT of the ZrO_2 and ZYZ films showed a sudden drop at a similar physical oxide thickness (POT) of ~ 3.5 nm, whereas that of the ZAZ curve showed a similar decrease at a much greater POT (~ 6.0 nm). The result evidently indicates that the minimum POT required for the crystallization of the top ZrO_2 layer during the PMA increased significantly on the Al_2O_3 layer, while the impact of the Y_2O_3 layer on the crystallization was almost negligible.

It is noteworthy that there was another transition point in the case of the ZAZ at ~ 7 nm, which might indicate the crystallization of the bottom ZrO_2 layer. This implies that even the bottom ZrO_2 layer had not been crystallized in the thinner ZAZ case due to the presence of the Al-doping, which was not the case in ZYZ. Although the Y_2O_3 insertion layer in ZrO_2 based dielectric did not inhibit the crystallization, the leakage current was still well suppressed (2.9×10^{-8} A cm^{-2} at 0.8 V, POT ~ 6.8 nm). ZYZYZ thin films exhibited the most stable and improved leakage current control among the tested candidates.

ALD Fundamentals

Room On Demand - Session AF1

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

AF1-1 Thermal Atomic Layer Deposition of Cobalt Metal Films: Synthesis and Characterization of Volatile, Thermally Stable Cobalt Precursors and Development of New Thermal Cobalt ALD Processes*, Nyi Myat Khine Linn,* *J. Hollin, Z. Devereaux, C. Winter,* Wayne State University

Miniaturization trends in microelectronics require thin films of transition metals and alloys by thermal atomic layer deposition (ALD), because thermal ALD can deposit ultrathin films with conformal coverage in high aspect ratio features and afford Angstrom-level thickness control. Recently, growth of cobalt metal thin films has gained attention due to numerous applications, such as replacing copper with cobalt in nanoscale devices. However, there have been limited reports of thermal ALD processes for cobalt metal because most cobalt precursors have low thermal stabilities (decompose at <250 ℃) and low reactivity toward common reducing agents. The overall goal of our project is the discovery of new cobalt ALD precursors and the development of new cobalt ALD processes. This cobalt process will be incorporated with other metal precursors to afford metal alloy thin films, such as $CoTi_x$ (x = 0.18-0.83). Different classes of cobalt(II) complexes, containing ligands such as β-ketoiminate, β-diketonates, and β-diketonate with neutral donors, were synthesized as potential ALD precursors. The volatility and thermal properties of these compounds were assessedby thermogravimetric analysis, melting point, and thermal decomposition studies. Cobalt metal ALD studies were carried out with substrate temperatures from 200 to 300 ℃ using a cobalt precursor and a nitrogen-based reducing agent. Cobalt nitride and cobalt metal films resulted. Film growth only occurred on metal substrates and not on insulators. Cobalt elemental composition on the substrates was first analyzed by X-ray photoelectron spectroscopy. Film thicknesses were measured by cross-sectional scanning electron microscopy and the phases of the films were characterized by grazing incidence X-ray diffractometry. Other film characterization data will be presented.

**AF1-2 Atomic Layer Deposition of Ga_2O_3 Thin Films Using a Liquid Precursor Pentamethylcyclopentadienyl Gallium and Combinations of H_2O and O_3*, Makoto Mizui*, *N. Takahashi, S. Higashi, F. Mizutani,* Kojundo Chemical Laboratory Co., Ltd., Japan

Pentamethylcyclopentadienyl gallium (GaCp*) is a liquid precursor for atomic layer deposition of Ga_2O_3 thin films. GaCp* is a cyclopentadienyl compound having a pentahapto half-sandwich structure as well as ethylcyclopentadienyl indium (InEtCp), which we previously reported [1]. Recently, we reported that high-purity Ga_2O_3 thin film with negligible carbon residue was deposited by the ABC-type ALD process with GaCp*, H_2O, and O_2 plasma (WpO) [2]. In this study, we applied O_3 as an alternative oxidant in place of O_2 plasma, and we conducted the ABC-type ALD process with GaCp*, H_2O, and O_3 (WOz).

The decomposition temperature of GaCp* was estimated to be around 250 °C by using differential scanning calorimetry. In our recent study of the WpO process, the growth temperature was set to 200 °C [2]. However, O_3 oxidization was supposed to be weaken below 200 °C [3]. Therefore, the growth temperature was set to 230 °C in this study. Ga_2O_3 thin films were deposited on 50 mm Si wafer with native oxide films. During the WOz process, linear growth with no incubation time and with a growth per cycle (GPC) of ~0.1 nm/cycle was observed, when 2 s GaCp*, 0.5 s H_2O, and 250 s O_3 pulse times were applied. For the WOz process, a self-limiting surface reaction occurred when a GaCp* pulse time of 1.5-3 s, a H_2O pulse time of 0.4-0.6 s, and an O_3 pulse time of 180-300 s were applied. With a short O_3 pulse time less than 180 s, oxidation was clearly insufficient and resulted in thinner Ga_2O_3 films. The GPC of the WOz process was larger than the GPC of WpO process (0.06 nm/cycle [2]). The reason was supposed that hydroxyl group remained after an O_3 step, and more reactive points existed at the next GaCp* step.

The elemental depth profile was analyzed by using high-resolution Rutherford backscattering spectroscopy (HR-RBS). It clearly shows that Ga_2O_3 film with a stoichiometric composition (O/Ga = 1.5) was obtained by WOz process, and that carbon was detected only on the surface. This result is comparable with the WpO process [2], and it indicates that ALD Ga_2O_3 film with high purity and negligible carbon residue was possible by using O_3 as an alternative oxidant in place of O_2 plasma.

The Ga_2O_3 films by ABC-type ALD with GaCp*, H_2O, and O_3 was demonstrated. This result will expand the potential of GaCp* for attractive applications such as large-area displays.

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AF1-3 Synthesis, Structure and Property Evaluation of a New Class of Volatile Lanthanide Precursors Containing Enaminolate Ligands*, C. Winter,* ***Navoda Jayakodiarachchi,*** Wayne State University

Thin films of binary lanthanide oxides and lanthanide-containing ternary oxides have gained increased attention in the microelectronics industry due to their high dielectric constants, large band gaps, and small lattice mismatches with silicon, which make them excellent materials for gate dielectrics in semiconductor devices. Also, lanthanide oxide thin films are useful as protective and antireflection coatings, luminescent materials, and catalysis. Atomic layer deposition (ALD), which is a thin film deposition technique that affords Angstrom-level thickness control and high conformality in high aspect ratio features, is a promising technique to deposit lanthanide oxide thin films. However, lanthanide precursors available to deposit lanthanide oxide thin films by ALD remain limited, especially for water-assisted lanthanide oxide processes. Hence, designing new lanthanide precursors for ALD is a crucial driving force for the advancement of microelectronic devices and also for accessing new properties and applications associated with lanthanide oxide materials. We have prepared a new class of lanthanide precursors containing enaminolate ligands of the formula $[R_2NCH=C(tBu)(O)]^-$ by treatment of three equivalents of the potassium enaminolate salt with one equivalent of anhydrous lanthanide(III) chlorides. As representative examples, La, Pr, Nd, Er, Lu, and Y complexes were synthesized and characterized using NMR, IR spectroscopy, and CHN microanalyses. The molecular structures of selected complexes were determined using X-ray crystallography. The volatility and thermal stability of the new complexes were evaluated using thermogravimetric analyses, sublimation temperatures, and thermal decomposition temperature measurements to determine their suitability as ALD precursors. To study the effect of the ligand substituents on the volatility and thermal stability of the lanthanide enaminolate complexes, three ligand derivatives with different R group were employed (L^1, $NR_2 = N(CH_3)_2$, L^2, $NR_2 = N(CH_2)_4$, L^3, $NR_2 = N(CH_2)_5$). All of the lanthanide enaminolate complexes were volatile and sublimed between 95 and 160 °C at 0.5 Torr. Complexes with L^1 ligand showed the lowest sublimation temperatures (95 to 120 °C at 0.5 Torr), whereas complexes with L^2 and L^3 ligands sublimed at 140 to 160 °C at 0.5 Torr. Moreover, complexes with L^3 ligands showed higher thermal stabilities than those found in L^1 and L^2 complexes. Most importantly, these lanthanide enaminolate complexes were found to be reactive toward the water, which is a promising sign for the use of these precursors in future water-assisted ALD processes to deposit lanthanide-containing thin films.

AF1-4 Metal Selenides: From Precursor Synthesis to Atomic Layer Deposition

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Metal selenides possess interesting properties among various fields, as photovoltaics, thermoelectric materials, photocatalysis and many other. ALD is a technique that allows for film deposition of these materials with nanometer thickness, and which can even enhance the desired characteristics. Solution Atomic Layer Deposition (sALD) is an emerging method bypassing some of the gas ALD (gALD) limitations, and in which the gas-solid reaction system is substituted with reactions between the substrate surface and precursors dissolved in appropriate solvent.

The literature provides very few chemical methods for the controlled deposition of metal selenides. Essentially, the number of potential selenium precursors for deposition represents a bottleneck. Besides the highly toxic and unstable H_2Se, only bis(trialkylsilyl)selenides are established for selenides thin film manufacturing. This work presents various silyl- and stannylselenides with linear or cyclic structure for gALD and sALD depositions. The molecular structures can be tailored to achieve various trade-offs between volatility, reactivity, air stability or ease of synthesis, as required depending on the application.

Selected precursors are then tested in gALD and sALD to prepare metal selenides and compared. Both the choice of precursor molecule and the choice of technique (gALD vs sALD) can be used to adjust the results and optimize them towards either high growth or high substrate selectivity.

AF1-5 Investigating the Role of Sigma and Pi Bonding in Volatile Molybdenum(Vi) Precursors

Michael Land, *G. Bačić,* Carleton University, Canada*; K. Robertson,* Saint Mary's University, Canada*; S. Barry,* Carleton University, Canada

Several atomic layer deposition (ALD) processes that deposit molybdenum films use precursors with the bis(tert-butylimido)molybdenum(VI) framework. Most of the reported volatile molybdenum compounds are prepared via salt metathesis reactions of bis(tert-butylimido)dichloromolybdenum(VI) ($(tBuN)_2MoCl_2$) with anionic nitrogen-based ligands such as dimethylamide or amidinates. Recently, we investigated the volatility and thermal stability of the parent compound, $(tBuN)_2MoCl_2$, and the effect of neutral ligands including amines, phosphines, ethers, and carbenes [1]. Some of the coordinating ligands increased the volatility of this framework but were found to dissociate from the metal complex upon evaporation. This "ligand-assisted volatilization" is a convenient method to increase the volatility of a compound for purification (by sublimation) purposes but is not practical for ALD since ligand dissociation in the gas phase will cause inconsistent gas-phase concentrations.

Notably, the neutral N,N'-chelate ligands did not dissociate from the metal complex upon heating. Herein, we investigate a series of $(tBuN)_2MoCl_2$ complexes with neutral N,N'-chelates. Incorporation of 1,4-di-tert-butyl-1,3-diazabutadiene results in a volatile compound (**1**) with an onset of volatilization of 91 ºC (from thermogravimetric analysis, Fig. 1) and thermal decomposition beginning around 170 ºC, (from differential scanning calorimetry). We found we could easily increase the thermal stability as we proceed down the spectrochemical series towards "low spin ligands". For example, the corresponding 2,2'-bipyridine adduct (**2**), has a significantly increased thermal stability, with an onset of decomposition at 240 ºC. Although this increased stability comes at the cost of volatility (165 ºC); however, a similar thermal range (79 ºC for **1** and 75 ºC for **2**) is observed.

Several other ligands were also investigated with thermal stabilities ranging from 160 ºC for "higher spin ligands" to 273 ºC for "lower spin ligands". Increases in thermal stability appear to arise from a π-withdrawing effect, whereas decreases arise from a σ-donation effect: these opposing bonding effects were investigated computationally. These effects reduce and increase the basicity of the imido nitrogen atom, respectively, which controls the activation energy for the primary decomposition pathway; γ-H activation of the tert-butyl group (Fig. 2). Finally, all compounds have been characterized in the solid state, using traditional spectroscopic techniques, including single-crystal X-ray diffraction.

AF1-6 Unearthing Zinc Alkyls as Reducing Agents in Cobalt Metal ALD: Mechanistic Studies, Process Development and Thin Film Analysis

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Cobalt-containing thin films and nanomaterials – in particular metallic Co – are garnering significant interest as next-generation interconnects to replace Cu in future nanoelectronic devices. A review of the current ALD processes for Co thin films reveals a surprising gap: No studies on the use of metal organic reducing agents has been reported.[1] This is surprising considering the ALD history of its "competitor" Cu and the reports on processes employing several Cu(I) and Cu(II) precursors being reduced with the well-known $Zn(Et)_2$.[2,3] However, deposition of copper using this Zn-containing reductant resulted in unwanted Zn contamination owing to the low thermal stability and CVD-type behavior of $Zn(Et)_2$.[4]

This presentation describes the development of an ALD process yielding Zn-free thin films of Co, employing $CoCl_2$(TMEDA) (previously used in the ALD of Co_3Sn_2 intermetallics[5]) as Co precursor and $Zn(DMP)_2$, an intramolecularly stabilized Zn(II) aminoalkyl compound,[6] as Zn precursor. The precursor pair has been chosen based on an initial reactivity study encompassing several Zn precursor candidates (Figure 1) which allowed us to hypothesize the mechanistic reaction steps that may be involved in thin film growth in the ALD process. The mechanisms of thin film formation are examined by detailed DFT calculations to support the proposed reaction paths.

A full process study was carried out on 2 inch Si(100) wafers (Figure 2).Typical ALD growth characteristics in terms of saturation were found for both Co and Zn precursor pulse and a strong dependency of the growth per cycle (GPC) on the deposition temperature was observed. The film thickness scaled linearly with the number of deposition cycles, confirming ALD behavior. Complementary RBS/NRA and XPS investigations on selected Co thin films confirmed their metallic nature and the absence of Zn. While other impurity levels were low as well, the C contamination amounted to 20 at.%. Nevertheless, resistivity measurements of Co thin films directly grown on insulating SiO_2 substrates yielded promising values of 15 - 20 µΩ cm.

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AF1-7 Deposition of Dielectric Y_2O_3 Thin Films by Thermal ALD Using a Homoleptic yttrium Formamidinate Precursor and Water

Nils Boysen, *D. Zanders, T. Berning, D. Rogalla, S. Beer, C. Bock, A. Devi,* Ruhr University Bochum, Germany

The atomic layer deposition (ALD) of Y_2O_3 thin films is widely known to be an important process not only for the application of Y_2O_3 as high-*k* oxide, but also for wear-, corrosion-resistive and hydrophobic coatings. These applications benefit from the intrinsic properties of ALD processes such as a high thin film uniformity, conformality and compositional quality. Such beneficial properties can only be exploited if the precursor chemistry and behavior is fine-tuned for a thoroughly optimized ALD process. In this study, we opted for the development of an ALD process for the formation of dielectric Y_2O_3 thin films using a homoleptic yttrium precursor $[Y(DPfAMD)_3]$ and compared the chemical nature of the precursor, ALD process characteristics and the resulting thin film quality to the already established processes using the parent amidinate $[Y(DPAMD)_3]$ and guanidinate $[Y(DPDMG)_3]$ precursors. Thermogravimetric analysis (Figure 1) of all compounds revealed superior evaporation behavior of $[Y(DPfAMD)_3]$ compared to $[Y(DPAMD)_3]$ and $[Y(DPDMG)_3]$, which ultimately resulted in considerably reduced precursor evaporation temperatures of only 95 °C in the corresponding ALD process and an enhanced ALD processing window reaching from 200 °C to 325 °C (Figure 2). Homogeneous, smooth and crystalline thin films were obtained at 300 °C with a GPC of 1.36 Å and contamination levels (C and N) were under the detectable limits of NRA (< 0.5 at.%) at this deposition temperature. XPS confirmed the low levels of impurities on the surface of the films and interesting similarities and differences were found in the O1s and Y3d core level spectra, where the contribution from yttrium hydroxides (Y-OH) as an intrinsic feature of the water assisted ALD process are possibly lower when using $[Y(DPfAMD)_3]$ compared to $[Y(DPAMD)_3]$ and $[Y(DPDMG)_3]$. The quality of the Y_2O_3 thin films was tested in metal-insulator-semiconductor (MIS) device structures, where a high permittivity of 13.9 at 1 MHz and a low breakdown field in the range of 4.2 to 6.1 MV cm^{-1} could be determined. The presented results clearly show that a rational choice of the precursor and only small changes within the ligand sphere of the precursor can have a considerable impact on its performance in the corresponding ALD process.

AF1-8 $(^{t}BuNH)SiMe_2NMe_2$ – a new *N,N′*-κ_2-monoanionic Ligand for Atomic Layer Deposition Precursors*, Matthew Griffiths,* Carleton University, Canada*; D. Zanders,* Ruhr University Bochum, Germany*; M. Land,* Carleton University, Canada*; J. Masuda,* Saint Mary's University, Canada*; A. Devi,* Ruhr University Bochum, Germany*; S. Barry,* Carleton University, Canada

Thanks to ALD precursor design research, today there exist volatile and thermally stable precursors for almost every element on the periodic table. While this has enabled materials of all different types to be deposited, there are still some shortcomings that arise from the incorporation of impurities into the deposited films. In many cases, these impurities are not only detrimental to the properties of the film, but they are introduced from the metalorganic precursor itself.

Amidinate precursors are one of the most popular classes of ALD precursor because they are easily synthesized and react cleanly with most co-reagents to deposit metal oxides, nitrides, sulfides, and other binary or ternary materials. In some cases, however, forming a metallic film using metal amidinates and a reducing co-reagent can leave significant amounts of carbon and nitrogen in the films. This has prompted a revitalized push to develop new precursors for refractory metals and many of the first-row transition metals. We hypothesized that a potential improvement to the amidinate system could be to make it slightly less strongly bound to the metal center by disrupting the resonance structure present in the ligand and thus allow for reduction on a surface to proceed more readily.

To furnish a stable ligand, we replaced the bridgehead carbon of the amidinates with silicon, giving a *gem*-diaminosilane (gDAS) which has the desired *N,N′*-κ_2-chelating motif and is monoanionic like the amidinates. The ligand $(^{t}BuNH)SiMe_2NMe_2$ (R^1 = Me, R^2 = ^{t}Bu) has been described only once for the first-row transition metals (Ni and Co); thus we decided to explore its potential across the periodic table.

Two Li compounds have been identified and perform well by thermogravimetric analysis (TGA). Due to the large steric bulk of this ligand, complexes that would contain more than two gDAS ligands have not been observed (Sc and Ti). When attempting to prepare $V(gDAS)_3$ we instead isolate only $V(gDAS)_2$. This +2 oxidation state is common for many of the first-row transition metals and this ligand forms thermally stable and volatile precursors of the type $M(gDAS)_2$. Where M = V, Mn, Fe, Co, Ni, Zn, and Mg, the compounds perform exceptionally well with residual masses by thermogravimetric analysis (TGA) below 5%, and 1 Torr temperatures between 110 and 115 °C. In particular the $Co(gDAS)_2$ complex is very thermally robust and performs very well during a TGA stress test. These compounds are the first of a family of precursors containing this type of monoanionic N-Si-N ligand and are prime candidates for ALD process development.

AF1-9 Aluminum Hydride Precursors for Atomic Layer Deposition of Aluminum Metal*, C. Winter,* ***Nilanka Sirikkathuge,*** Wayne State University

The growth of atomically precise, conformal aluminum (Al) metal films is desired due to their applications in microelectronics, plasmonics, energetic materials, and hydrogen storage processes. Thermal atomic layer deposition (ALD) can be employed to grow high-quality films through sequential and self-limiting surface reactions. Al metal possesses a very negative electrochemical potential ($Al^{3+} + 3e^- \leftrightarrow Al$, E^o = -1.676 V), which necessitates the use of powerful, thermally stable reducing agents as co-reactants during thermal ALD processes. There have been only two literature reports on the thermal ALD of Al metal films, both of which came from our laboratory. Considerable work remains to be carried out to develop strongly reducing co-reactants that can be used for Al metal ALD. In the present work, we will describe the synthesis, characterization of Al dihydride complexes of the formula $[LAlH_2]_n$ where L is a monoanionic, multidentate oxygen or nitrogen ligand. The applicability of these complexes as reducing agents in the thermal ALD of Al and other metal deposition processes will be overviewed.

AF1-10 Growth Mechanism of the Atomic Layer Deposition of ZnO Thin Films Using Bis(*n*-Propyltetramethylcyclopentadienyl)Zinc*, Fumikazu Mizutani,* *M. Mizui, N. Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M. Inoue, T. Nabatame,* National Institute for Materials Science, Japan

We have reported the atomic layer deposition zinc oxide thin films using cyclopentadienyl-based precursors, bis(*n*-propyltetramethylcyclopentadienyl)zinc, $Zn(Cp^{pm})_2$, which is expected to deposit high-purity ZnO thin films [1]. At that time, ZnO thin films were deposited at 200 °C on 150 mm Si wafers with native oxide films, and the ALD process consisted of alternating exposure to $Zn(Cp^{pm})_2$ and oxidants, H_2O followed by an O_2 plasma. Then, linear growth up to 50 cycles was observed with pulse times for $Zn(Cp^{pm})_2$, H_2O, and O_2 plasma of 0.1, 30, and 120 s, respectively [1].

However, after that, when the sample deposited up to 1000 cycles was analyzed by cross-sectional TEM, it was found that the film of SiO_2 containing a small amount of Zn was initially grown, and the island-shaped ZnO film was grown in the next stage. That is, since the precursor is adsorbed at a low density in the initial stage, it is considered that the SiO_2 film grew while taking in Zn in the precursor by O_2 plasma having a very long pulse time. And at the next stage, nucleation has started. In the ALD process design, the precursor pulse, H_2O pulse, and O_2 plasma pulse correspond to precursor adsorption, precursor oxidation, and surface hydroxyl group dehydrogenation, respectively. Among these, the H_2O pulse time and the O_2 plasma pulse time are quite long, so it is considered that the cause of the nucleation delay was insufficient precursor pulse time. On the other hand, since the ZnO film is deposited after nucleation, it seems that the extension of the precursor pulse time is sufficient only at the initial stage. Therefore, the precursor pulse time was extended to 1 s only in the first 10 cycles, and then ALD was performed up to 300 cycles with a precursor pulse time of 0.1 s to prepare a sample for evaluation of nucleation. When a cross-sectional TEM observation of this sample was performed, a conformal film was deposited. Thus, ALD without nucleation delay using this $Zn(Cp^{pm})_2$ was demonstrated.

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AF1-11 Ultrasonic Atomization of Titanium Isopropoxide at Room Temperature for TiO_2 ALD Thin Films*, Moon-Hyung Jang,* *Y. Lei,* University of Alabama in Huntsville

Room temperature evaporation of titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$, TTIP] precursor was performed using ultrasonic atomization technique for TiO_2 atomic layer deposition (ALD) thin films growth. Quartz crystal microbalance data show comparable results on the growth behavior between room temperature TTIP ultrasonic atomization and heated TTIP bubbler at 70 °C. The TiO_2 ALD saturation window is established for room temperature atomized TTIP exposure time and reactor temperatures. Room temperature atomized TTIP grown TiO_2 films show smooth surface morphology as well as TiO_2 anatase crystal structure before/after the annealing treatment. Two-dimensional TiO_2 film thickness mappings on a 150 mm diameter Si(100) wafer were performed by spectroscopic ellipsometry. The thickness variation of TiO_2 films by the room temperature atomized TTIP is less uniform than that of TiO_2 films by thermally vaporized TTIP, due to the incomplete evaporation of the TTIP liquid droplets, which is more difficult to transport than its vapor in the cross-flow configuration of ALD.

AF1-14 Designing Volatility Into Lead Precursors, *Goran Bacic*, Carleton University, Canada; *J. Masuda,* St. Mary's University, Canada; *S. Barry,* Carleton University, Canada

Volatility is a critical property of ALD precursors, but there is no reliable method to predict it. This was recently highlighted in our research when we discovered that bis[lead(II) *N,N′*-di-*tert*-butyl-1,1-dimethylsilanediamide] [(**4Pb**)$_2$] had good volatility (112°C/1Torr) despite being dimeric in the solid and vapor phases. Oligomerization usually decreases volatility, so we attempted to cleave the dimer to improve volatility by increasing steric bulk, adducting the monomer with a Lewis base, and by installing a pendant tertiary amine onto the ligand itself. None of these strategies produced a more volatile complex than (**4Pb**)$_2$. Indeed, even the monomeric derivative lead(II) N,N′-bis(1-(dimethylamino)-2-methylpropan-2-yl)-1,1-dimethylsilanediamide (**5Pb**) had slightly lower volatility (118 °C/1Torr). These counter-intuitive results led us to investigate the origins of high volatility with density functional theory (DFT) and experimentally with thermogravimetric analysis (TGA). In this talk, we will introduce and discuss our efforts to combine theoretical and experimental methods to predict precursor volatility.

Since volatility is governed by intermolecular interactions, which in turn are determined by the molecular electrostatic potential (ESP), we modeled vapor pressure against statistical properties of the ESP. To fit our models, we obtained a consistent set of measured vapor pressures for several known and novel lead precursors: the novel (**4Pb**)$_2$ and **5Pb** were compared to the recently reported acyclic lead(II) bis[bis(trimethylsilyl)amide] (Pb(btsa)$_2$, 127°C/1Torr) and the cyclic lead(II) *rac-N,N′*-di-*tert*-butyl-2,3-diamidobutane (**1Pb**, 94°C/1Torr), as well as more classical precursors (e.g., Pb(tmhd)$_2$, 166 °C/1 Torr). For the theoretical calculations, we developed an efficient and reliable DFT methodology (ωB97X-D3(BJ)//revPBE) which was benchmarked against high-level ab initio coupled-cluster calculations (DLPNO-CCSD). Statistical analysis revealed strong correlations between vapor pressure and the total variance ($\sigma_{\pm}^2$, R^2= 0.987), absolute polar surface area (*A*, R^2= 0.983), and standard deviation ($\prod$, R^2= 0.970) of the ESP. With these results, we were able to explain how dimerization improves the volatility of (**4Pb**)$_2$, why the monomeric **5Pb** was less volatile, and which hypothetical lead precursors may be more volatile. Finally, we generalize our findings to qualitative design considerations, critically evaluate the limitations of our current approach, and outline the path toward a quantitative methodology to predict volatility.

AF1-17 Solution ALD: A Versatility Process for Various Material Growth, *Maissa Barr*, *B. Zhao, P. Von Grundherr, M. Uddin, V. Koch, M. Halik, J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

We have proposed and demonstrated a novel thin film deposition technique by transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, towards precursors dissolved in a liquid. The technique can also be considered as a generalization of already established methods such as the 'layer by layer' growth or the 'successive ion layer adsorption and reaction' (SILAR). 'Solution ALD' (sALD) shares the fundamental properties of standard 'gas ALD' (gALD), specially the self-limiting growth and the ability to coat conformally deep pores. It has been already shown that it is possible to transfer standard reactions from gALD to sALD such as TiO_2 deposition . However, sALD also offers novel opportunities such as overcoming the need for volatile and thermally robust precursors.

To illustrate this, we establish sALD procedures for depositing films of non oxides layers such as Pb-compound deposition, MOF, selenides and sulfides. Those examples highlight how ionic, polar, or high-molecular weight precursors that only exist in the condensed phase are now rendered amenable to being utilized in surface-controlled thin film formation by sALD for depositing materials that would otherwise be more difficult or more expensive to achieve by gALD or hazardous. The deposition was achieved on small (2 cm*1 cm) and large samples (up to 10 cm*10 cm). The ALD behavior has been shown. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition has been investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. Additionally, the nucleation is studied in function of chemical pretreatment to control the gowth and allow selective deposition of CuS, ZnS and SnS.

This particular ALD process offer the growth of high quality and crystalline layers in middle conditions with the use of low cost and environmental friendly precursors.

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AF1-20 Routes to Novel Dielectric and Semiconductor Devices Using Cyclohexasilane, *Ramez Elgammal,* The Coretec Group

A newly developed "liquid silicon" precursor will be discussed. Cyclohexasilane (CHS; Si6H12) has been used to make silicon-based films (such as polysilicon, silicon nitride, silicon carbide and others), as well as silicon nanowires and quantum dots. CHS offers a more versatile, lower-cost and safer pathway to a variety of silicon based products being considered for flexible and printable electronics. One particularly interesting deposition method for CHS that has recently received interest is ALD.

There is a need for a silicon precursor that is not only cost effective, but one that can be readily chemically functionalized to develop advanced materials. CHS is one such silicon precursor that is a liquid at room temperature allowing for easier storage and handling. Cyclohexasilane has a moderate boiling point, 80 °C at 15 torr. It has long been considered to be the preeminent silicon precursor for a variety of applications including silicon anodes, solid state lighting, and a wide variety of semiconductor devices. CHS may also be used to create thin films of β-SiC on a variety of substrates under mild conditions.

Aside from those advantages, CHS allows for facile p-doping of materials and due to the methods of deposition and the deposition conditions amenable to a reagent such as CHS, continuous growth with the suppression of unintentional secondary deposits may be readily achieved. Moreover, it may be possible to use CHS to achieve solution growth to deliver high structural quality materials with significantly decreased capital and operational costs.

The use of CHS across a wide range of industries and applications will be discussed as will the advantages of this material over incumbent technologies.

AF1-23 Atomic Layer Deposition of Cupric Oxide Using Copper(II) Acetylacetonate, *Gabriel Bartholazzi, L. Black,* The Australian National University, Australia

Copper oxide is a well-known p-type semiconductor with potential applications in a range of fields, including photovoltaics, gas sensors, catalysis and water splitting. It is mainly found in two oxidation states, cupric oxide (CuO) and cuprous oxide (Cu_2O). In some applications, Cu_2O is preferred due to its larger bandgap of 2.1-2.6 eV compared to 1.3-17 eV for CuO. Cu_2O has been previously deposited by ALD using various combinations of precursors and reactants such as $Cu(OAC)_2$ and H_2O, $^{n}(Bu_3P)_2Cu(acac)$ and wet oxygen and Cu(I)(hfac) and H_2O. However, the copper precursors used in these processes suffer from some drawbacks such as poor stability ($Cu(OAC)_2$),adhesion problems due to fluorination (Cu(I)(hfac)) and small temperature window ($^{n}(Bu_3P)_2Cu(acac)$). Copper(II) acetylacetonate ($Cu(acac)_2$)appears to be a promising candidate due to its high stability, relatively low price and vapour pressure. Additionally, reports have shown that this precursor has a wide deposition window which is a very important feature when depositing in combination with other materials. $Cu(acac)_2$ has been reported in combination with O_3 to produce CuO and in a supercycle reaction with H_2O and a reducing agent to produce Cu. Conversely, the $Cu(acac)_2/H_2O$ process was reported not to result in film growth. Cu_2O films obtained from $Cu(acac)_2$ by ALD have yet to be reported. In this work, we demonstrate ALD of Cu_2O from $Cu(acac)_2$ and a combination of H_2O and O_2 as reactants. The depositions were carried out using a Beneq TFS-200 system. Double-side-polished silicon wafers were used as substrates. The $Cu(acac)_2$ precursor was held at 140°C. The precursor and reactant pulse times were varied in order to obtain the process saturation curves. Ex-situ spectroscopic ellipsometry was used to determine the film thickness and optical constants. Fourier-transform infrared spectroscopy (FTIR) and grazing incidence X-Ray diffraction (GIXRD) were used to determine the crystallinity and oxidation state. Film uniformity and roughness were assessed using atomic force microscopy. The results confirm self-limiting deposition behaviour with a growth per cycle of ~0.07 Å/cycle at 200°C. The relatively low growth rate may be due to the incomplete reaction of the precursor ligands, as some level of carbon impurities were detected by FTIR. Nevertheless, GIXRD and FTIR confirm that the desired Cu_2O oxidization state was obtained using this process. Films are crystalline and present a direct band gap of 2.6 eV.

The final submission will include additional results on the process optimization which are to be completed soon.

AF1-26 Low-Temperature Growth of Crystalline Tin(II) Monosulfide Thin Films by Atomic Layer Deposition Using a Liquid Divalent Tin Precursor*, **Mohd Zahid Ansari,*** Yeungnam University, Korea (Republic of)*; P. Janicek,* University of Pardubice, Czechia*; D. Nandi,* Yeungnam University, Korea (Republic of)*; S. Slang, M. Bouska,* University of Pardubice, Czechia*; H. Oh,* Yeungnam University, Korea (Republic of)*; B. Shong,* Yeungnam University, Czechia*; S. Kim,* Yeungnam University, Korea (Republic of)

Better-quality stoichiometric SnS thin films were prepared by atomic layer deposition (ALD) using a novel liquid divalent Sn precursor, N, N′-di-*t*-butyl-2-methylpropane-1,2-diamido tin(II) [Sn (dmpa)], and H_2S. A relatively high growth per ALD cycle (GPC) value of approximately 0.13 nm/cycle was achieved at 125 °C. Crystalline SnS films could be grown from room temperature (25 °C) to a high temperature of 250 °C. Density functional theory calculations were used to examine the surface reactions and self-limiting nature of the Sn precursor. Mixed phases of cubic (π) and orthorhombic (o) SnS films were deposited at low temperatures (25–100 °C), whereas only the orthorhombic phase prevailed at high growth temperatures (>125 °C) based on the complementary results of XRD, Raman spectroscopy, and XPS analyses. The optoelectronic properties of the SnS films were further evaluated by spectroscopic ellipsometry(SE) analysis. The results from the SE analysis supported the observed change from mixed π-SnS and o-SnS to o-SnS with increasing deposition temperature and allowed the determination of the energy bandgap (∼1.1 eV) and a relatively broad semi-transparent window (up to 3000 nm). Overall, this new ALD process for obtaining a good quality SnS is applicable even at room temperature (25 °C), and we foresee that this process could be of considerable interest for emerging applications.

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ALD Fundamentals
Room On Demand - Session AF10
ALD Fundamentals Poster Session

AF10-1 Datasets and Algorithms for Machine Learning-Driven Process Optimization Using ALD Growth Profiles*, **Angel Yanguas-Gil,** J. Elam,* Argonne National Laboratory

Process optimization is a crucial aspect of atomic layer deposition that is often carried out through a combination of trials and human expertise. In this work we explore how machine learning approaches, and in particular artificial neural networks, can help accelerate such optimization, potentially reducing it to a two step process.

Our goal is to use thickness values measured at different points of a reactor as well as dose timings as inputs to predict optimization targets such as dose times required to achieve full saturation or predicting growth profiles in areas that are not readily accessible. This data is usually obtained as part of the routine characterization process after each deposition. Our approach relies on two steps: we first use CFD simulations to generate growth profiles inside a reactor of a given geometry. The simulations depend on parameters that are generally not known, but when enough conditions are explored, they provided a dataset that covers the expected behavior of a wide range of ALD process. The resulting datasets are split into two different sets, one for training, and one for training, so that machine learning algorithms can be validated against data they have not been trained against. The second step is to train surrogate models using the training datasets to carry out a specific task. In this work we have explored primarily models based on artificial neural networks.

When trained and compared for tasks such as predicting saturation times, machine learning models based on artificial neural networks can accurately predict dose times, with a Pearson correlation accuracy exceeding 0.99 with respect to the testing dataset. When we apply this model to experimental data obtained for TMA/water growth in our cross flow reactors we also observe similarly a very good accuracy. We have generalized this model to situations involving more than one growth conditions, therefore extending the models to conditions where we are trying to optimize both saturation times simultaneously. Finally, we explore other relevant problems, such as the discrimination between self-limited and non-self limited growth, which can be casted as a classification task, and the case of process transfer across two different reactors.

AF10-2 Conducting Hafnium Nitride Films Fabricated by Atomic Layer Deposition With Cleaning Step and Post-Deposition Annealing in NH_3 Atmosphere*, **Seung Kyu Ryoo,** B. Kim, H. Park, Y. Lee, S. Lee, M. Oh, I. Lee, S. Byun, D. Shim, C. Hwang,* Seoul National University, Korea (Republic of)

As the scaling down of memory device kept proceeded, a highly integrated structure using high-*k* gate dielectrics (such as HfO_2) has attracted a great deal of interest to ensure high performance in the ultra-thin film (<10 nm). At the same time, HfO_2 compatible electrodes are also required to reduce degradation caused by the adverse interface properties between electrode and dielectric. Among various materials, hafnium nitride (HfN) is one of the most promising candidates, with superior compatibility with HfO_2, low bulk resistivity, and high thermal stability. For high-density memory application, all layers in the memory cell (dielectric, electrode) should be fabricated by atomic layer deposition (ALD) for conformal growth. However, it is challenging to obtain conductive hafnium nitride films grown by ALD because of the formation of the insulating phase (Hf_3N_4) or contamination of oxygen impurity (HfO_xN_y).

In this study, conducting hafnium nitride film with a low impurity (<5%) was deposited by ALD and post-deposition anneal (PDA). The ALD HfN films were deposited using TEMA-Hf($[HfN(CH_3)C_2H_5]_4$) as a Hf-precursor- and NH_3 as a reactant gas. The cleaning step, feeding only TEMA-Hf without NH_3 gas, was conducted before the main ALD cycle to decrease the impurity concentration in the grown hafnium nitride thin films. During this step, injected TEMA-Hf reacted with impurities and decreased the residual contamination gases inside the chamber without being deposited on the substrate. The PDA at temperature >900℃ under the NH_3 atmosphere further decreased impurities and promoted phase change from insulating Hf_3N_4 to conducting HfN. Finally, HfN film with a resistivity of 10^6μΩ·cm could be achieved by such process optimizations.

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AF10-3 Higher Temperature ALD for HfO_2 Film using Hafnium Aminoalkoxide Precursors*, **Masako Hatase**, H. Sato, A. Sakurai, T. Yoshino, N. Okada, A. Nishida, A. Yamashita,* ADEKA CORPORATION, Japan

Hafnium oxide (HfO_2) is widely used in the semiconductor industry as a high-k dielectric in memory capacitors and as a gate insulator in field effect transistors. Recently, HfO_2 attracts additional attention as a possible candidate for CMOS-compatible and scalable ferroelectric memories. The properties of HfO_2 films vary depending on the crystallographic structures which can be controlled with deposition conditions. For example, higher deposition process is promising to obtain a higher dielectric constant phase. For the last decade or more, hafnium amide-, cyclopentadienyl- and chloride-based precursors have been commonly used as ALD precursors, but their thermal stabilities are insufficient for higher temperature use. Therefore, more thermally robust hafnium precursors for higher temperature ALD are considered to be advantageous.

In this work, several hafnium aminoalkoxide precursors have been investigated. As general hafnium alkoxide precursors [$Hf(OR)_4$] have unoccupied cordination sites, we have introduced amine chelates in the molecule to complete the hafnium coordination sphere. Tetrakis(1-dimethylamino-2-propoxy)hafnium [$Hf(dmap)_4$] is a viscous liquid at room temperature and has high vapor pressure (1.0 torr @ 153°C). The thermal stability of $Hf(dmap)_4$ was found to be higher than that of TDMAH by 90°C according to DSC measurement. We demonstrated ALD of HfO_2 using $Hf(dmap)_4$ with an O_3 coreactant. Self-limiting film growth on Si and SiO_2 substrates was observed at higher deposition temperature from 250°C to 350°C. A smooth HfO_2 film was confirmed by FE-SEM measurement (Fig. 2). Furthermore, carbon and nitrogen contamination in the HfO_2 film was not detected by XPS measurement when deposited at 375°C (Fig. 3). We have also synthesized Tetrakis(1-dimethylamino-2-butoxy)hafnium [$Hf(dmab)_4$] and Tetrakis(1-ethylmethylamino-2-propoxy)hafnium [$Hf(emap)_4$], which are both thermally stable as well.

In conclusion, hafnium aminoalkoxide precursors are thermally robust and suitable for high temperature ALD of HfO_2 films. During the presentation, basic properties of the hafnium aminoalkoxide precursors and HfO_2 film quality will be discussed.

AF10-4 Plasma Enhanced Atomic Layer Deposition (PEALD) of Nickel Using Allyl Cyclopentadienyl Nickel as the Precursor, *Elham Kamali Heidari*, *K. Bosnick, J. Canlas, T. Patrie,* National Research Council, Canada

Owing to their excellent magnetic properties, low electrical resistivity, high thermal conductivity, high Curie temperature, excellent corrosion resistance and unique catalytic properties, nickel thin films and nanoparticles have found various applications ranging from information storage devices and electronics to energy storage, magnetic sensors and catalysis.

In the present study nickel thin films were deposited on silicon and sapphire substrates using allyl cyclopentadienyl nickel ($C_8H_{10}Ni$) as the precursor and N_2 and N_2/H_2 as the co-reactant plasma. This precursor was chosen due to its low melting point of 9 ^oC and high vapor pressure that provides the possibility of low temperature atomic layer deposition of nickel. PEALD was carried out by sequential exposure of the substrate to the precursor and plasma, followed by a purging time of 2 and 5s, respectively. The effect of substrate temperature as well as plasma composition and dose time was studied. X-ray reflectometry (XRR) studies showed that 200 ^oC is the optimum substrate temperature in terms of film thickness. Lower and higher temperatures resulted in a decrease in growth rate. Regarding the plasma composition, pure N_2 plasma leads to higher growth rates, but less Ni content in the film, while introducing 5% H_2 to the plasma results in lower growth rates but higher Ni concentrations. The optimum plasma does time is 15s. Lower dose times resulted in lower growth rates, while higher does times did not make changes to the thickness.

Finally, the optimum ALD Ni coated substrates were loaded in a CVD chamber for deposition of CNTs where Ni acts as the catalyst for nucleation and growth of CNTs. The scanning electron microscopy (SEM) as well as Raman spectroscopy studies showed that regardless of the plasma composition, CNTs are uniformly deposited all over the surface, showing the high effectiveness of the developed ALD process for deposition of well dispersed of Ni catalysts on the surface of both Si and sapphire. We believe the developed recipe can be applied for deposition Ni nanoparticles or thin films on different substrates for catalysis applications.

AF10-5 Enhancement of Ferroelectric Properties of $Hf_{0.5}Zr_{0.5}O_2$ Thin Films by Various Metal Electrodes, *In Soo Lee*, Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Seoul National University, Korea (Republic of); *B. Kim, S. Hyun, H. Park, Y. Lee, S. Lee, M. Oh, S. Ryu, S. Byun, D. Shim, C. Hwang,* Seoul National University, Korea (Republic of)

Since the discovery of ferroelectric properties in HfO_2-based materials, $Hf_{0.5}Zr_{0.5}O_2$ (HZO) became one of the most prevalent ferroelectric thin films due to its excellent ferroelectricity with small film thickness and CMOS-compatibility [1]. Among various metal electrodes used as a bottom electrode, the HZO film showed the best ferroelectric properties when grown on the TiN bottom electrode [2]. However, a recent study revealed that the tungsten (W) metal electrode used as a bottom electrode and top electrode resulted in the highest remnant polarization (P_r). As a top electrode, W shows a low thermal expansion coefficient inducing an in-plane tensile strain to HZO film during rapid thermal annealing, facilitating the formation of o-phase [3].

In this study, ferroelectric HZO films were deposited by the atomic layer deposition (ALD) technique on the TiN and W bottom electrode. At the same time, Ru and TiN were used as top electrodes. The 10-nm-thick HZO film deposited on the W electrode with TiN as a capping electrode showed a substantial increase in the $2P_r$ value ($50.1\mu C/cm^2$), which increased by 31.4% compared to the case of conventional TiN/HZO/TiN films. Also, 10-nm-thick HZO film deposited on TiN electrode with Ru capping electrode showed an even higher $2P_r$ value ($63\mu C/cm^2$) at 4.6MV. Detailed characterization results for the interface structure and possible origin for such improvements will be presented.

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AF10-6 Simulating Ultrasmooth, Pinhole-free Thin Films with a Monte Carlo Model of Nucleation and Growth, *D. LaFollette,* University of Southern California; ***Kinsey Canova***, *J. Abelson,* University of Illinois at Urbana-Champaign

The architecture of advanced microelectronic devices requires vacuum-deposited films that are only a few nm thick, pinhole-free, and smooth. However, film growth by ALD or low-temperature CVD often follows the Volmer-Weber mode that begins with nucleation of discrete islands that grow until the substrate is covered ("coalescence"). Film thickness and roughness at coalescence depend on several factors including the nucleation rate and the growth rate. To show the effects of these two parameters alone, we construct a Monte Carlo model that simulates film morphology as a function of (i) the nucleation rate of hemispherical islands at random positions on the bare surface and (ii) the constant film growth rate on those islands. Simulated films resemble AFM images of real films and reveal a remarkable power law relationship between the RMS roughness and the ratio of the nucleation and growth rates.

We next derive an analytical model based on Poisson point statistics at coalescence. It formally predicts the same power law trend that is observed in the Monte Carlo simulation. Both models estimate the required rates to grow a film within set limits of total thickness, roughness, and coverage.

Simulation results are compared to experimental data for HfB_2 films during the onset of growth; these match closely during some time periods but not over the entire process. The deviations presumably arise from the simplifying assumptions in the Monte Carlo simulation, which includes no kinetic parameters apart from the constant nucleation probability and growth rate. Therefore, the simulation can also be used as a tool to indicate the likely presence of additional kinetic factors, e.g., surface diffusion, in the growth process.

AF10-7 Revisiting Process Optimization in Atomic Layer Deposition: Going Beyond Growth Rate, *Elham Rafie Borujeny*, *K. Cadien,* University of Alberta, Canada

Atomic Layer Deposition (ALD) is a promising nanofabrication technique for depositing thin layers of a wide range of materials with atomic-level control over thickness, remarkable uniformity over large areas, and exceptional conformality on patterned structures. Optimized ALD processes consist of self-limiting reactions that introduce reactants or precursors to the substrate surface one by one in a cycle resulting in formation of a monolayer of target material on the surface. Conventionally, such optimized ALD processes are achieved by growing a number of trial films while varying the dose and the purge timings of the ALD cycle and obtaining growth per cycle (GPC) in each case. Once a stable GPC is obtained, the corresponding dose and purge timings are considered to be optimized and ensure self-saturation. One of the limitations of such GPC-based optimization strategy is that it requires significant resources (energy, material, and time) to repeat the experiments and obtain optimized cycle parameters in all deposition temperatures or conditions. In this work, we demonstrate a fast and versatile strategy to obtain self-saturating ALD cycle parameters at any deposition temperature or condition without needing to grow trial ALD films and obtaining GPC. Through a few examples, we show that our optimization approach results in self-saturating cycle parameters consistent with the GPC-based optimization approach and makes the resources available to obtain not only self-saturating ALD process parameters but also process conditions that are fine-tuned to obtain films with superior structure, property, and functionality. We also demonstrate that our optimization approach can provide a unique tool to investigate and design in-situ doping strategies for ALD films. Examples of successful doping of ALD films of emerging materials by using our approach are also provided.

AF10-8 Surface Reaction of Nb_2O_5 RT-ALD Explained by Using Quartz Crystal Microbalance Measurements, ***Kazuki Yoshida***, *K. Saito, M. Miura, K. Kanomata, B. Ahmmad, S. Kubota, F. Hirose,* Yamagata University, Japan

Metal oxides are used as protective layers for metal components, organic electronics, and packaging films. Niobium pentoxide (Nb_2O_5) has been studied as protective layers for the cathode of the fuel cells. The ALD coated Nb_2O_5 exhibits excellent anti-corrosion[1]. However, a high-temperature process over 200 °C was necessary in the conventional technologies. Previously, we reported the room temperature (RT) ALD process of Nb_2O_5[2], but we have not discussed the detailed surface reaction in the RT-ALD process. In the present study, we use a quartz crystal microbalance measurement (QCM) to investigate its surface reaction, which enables the monitor of the quartz crystal surface mass variation during ALD. It is confirmed that the surface mass increased in the step-by-step mode, suggesting that the Nb_2O_5 was deposited in ALD mode. In this study, we discuss the surface reaction in the Nb_2O_5 RT-ALD from the surface mass variation.

A schematic of the RT-ALD surface mass variation monitoring system with a QCM sensor is shown in Figure 1. We used plasma excited humidified Ar as an oxidizing gas, *tert(*butylimido)tris(ethylmethylamido)niobium (TBTEMN) as precursors of Nb_2O_5. Any heaters or thermal sources were not installed to the chamber wall. TBTEMN container was warmed up around 80 °C to promote the niobium precursor evaporation. The exposure time of TBTEMN was 50 s, plasma excited humidified argon was 615 s. The evacuation steps of 180 and 60 s were inserted between TBTEMN and the plasma excited humidified argon exposure. For the QCM measurement, we used an ALD sensor (#750-717-G2, Inficon) with AT-cut quartz crystals which a resonance frequency was 6 MHz. The sampling rate was 2 Hz. The surface mass variation during the whole process was recorded in a data logger as voltage variation.

We confirmed the surface mass variation during 10 cycles of ALD. The mass variation curve exhibits the stepwise increase that indicates the ALD growth mode. To discuss the surface reaction in this process, we picked up a typical mass variation curve in 10 cycles, as shown in figure 2. The surface mass varied during the precursor adsorption and surface oxidization period. The number of reacted ligands of the precursor adsorption period is estimated as 2 or 3 from a mass variation ratio during one ALD cycle. In the conference, we propose a surface reaction model of Nb_2O_5 RT- ALD.

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AF10-9 Ir Studies on Low-Temperature Atomic Layer Deposition of Aluminum Nitride Using Plasma Excited Ammonia*, Kentaro Saito,* *K. Yoshida, K. Kanomata, M. Miura, B. Ahmmad, S. Kubota, F. Hirose,* 4-3-16 Jonan, Japan

Aluminum nitride (AlN) has been attracting much attention since it is also expected to be used as a gas barrier for organic light emitting diodes (OLEDs). In the conventional technologies, depositions of AlN were examined by chemical vapor deposition (CVD) and atomic layer deposition (ALD), although these were performed at a temperature of 200 °C and higher. A low-temperature deposition is demanded for flexible electronics since the OLEDs are not torelant to the high-temperature processes. In this study, the low-temperature ALD of AlN using trimethylaluminum (TMA) and plasma-excited ammonia is examined. We aim to modelize the surface reactions of the low-temperature AlN ALD with multiple internal reflection infrared absorption spectroscopy (MIR-IRAS).

A p-type Si substrate was used as a sample with a form of prism for MIR-IRAS. The size of the sample prism was 10×48 mm^2 whose resistivity was 10 Ωcm. The sample prism was set in an ALD reaction chamber. The prism was heated at 160 °C with a direct current passing. In the nitridation step, ammonia and argon were mixed with a volume ratio of 7 : 3, followed by being excited in a quartz tube with an RF power of 250 W and a frequency of 13.56 MHz. The flow rate of the mixed gas was 10 sccm. Ammonia molecules in the mixture were dissociated to NH radicals and fragments for the nitridation.

We observed the surface reaction to confirm the TMA adsorption on the AlN surface at 160 °C and examine if the plasma-excited ammonia causes nitridation on the TMA adsorbed surfaces. Fig. 1 shows IR absorbance spectra, measured from the TMA adsorbed surface with TMA exposures from 1000 to 200000 L at 160 °C. The presence of positive peaks at 2941, 2899, and 2830 cm^{-1} indicates that TMA was adsorbed on the surface at 160 °C. Fig. 2 shows IR absorbance spectra measured from plasma excited ammonia treated TMA adsorbed surface. The negative peaks at 2941, 2899, and 2831 cm^{-1} indicate the degeneration of hydrocarbon, which might be due to the nitridation. From this observation, we designed the process of AlN ALD and confirmed the AlN deposition by X-ray photoelectron spectroscopy. In the conference, we discuss the reaction model of AlN deposition based on the IR absorption spectra and XPS analysis.In the conference, we discuss the surface reaction of the low-temperature AlN ALD.

AF10-10 Atomic Layer Deposition of SiO_2 using BDEAS and O_3 as Precursor*, Yu-Hsuan Yu,* Taiwan Instrument Research Institute, National Applied Research Laboratories , Taiwan*; C. Kei,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Silicon dioxide (SiO_2) is a common dielectric material in silicon microelectronic devices owing to its relatively low dielectric constant and large band gap. Science the size of microelectronic devices become smaller as the complexity of structure increase, the requirement on thickness and uniformity of SiO_2 coatings become stricter. Atomic layer deposition is known for precise thickness control and excellent step-coverage, which is a good candidate to fabricate SiO2 thin film. In this study, We deposited silicon oxide (SiO2) film by ALD using bis(diethylamino)silane (BDEAS) and ozone (O_3) as precursors. The SiO_2 film was deposited at several different temperatures which from 200℃ to 350℃. The thickness of SiO2 was measured by ellipsometer and TEM. The growth rate of SiO2 is from 0.13 (200℃) to 0.93 (350℃) Å/cycle.

AF10-11 Effect of Plasma Time in Plasma-Enhanced Atomic Layer Deposition on Wet Etching Properties of Aluminum Nitride*, Heli Seppänen,* *H. Lipsanen,* Department of Electronics and Nanoengineering, Aalto University, Finland

Aluminum nitride (AlN) is a material with a combination of piezoelectric lattice, high direct bandgap and high dielectric constant, which makes it interesting for a wide range of applications in modern technology [1, 2, 3, 4]. Thin films of AlN can be grown with atomic layer deposition (ALD) with both thermal and plasma-enhanced (PEALD) processes. Patterning the AlN film is often required to achieve the wanted structure, however wet etching of ALD AlN is not a well-studied topic. ALD AlN films commonly have a lower crystal quality in comparison with other deposition techniques, e.g. sputtering, and are thus easier to wet etch with safer chemicals [5]. As different process parameters affect the properties of the deposited film, the effect on etch rate is unknown.

In this study the effect of ion bombardment during the growth of the AlN film on the etching properties is investigated by comparing thermally grown AlN to PEALD grown AlN with different plasma times. The AlN films are characterized using spectroscopic ellipsometry and X-ray diffraction (XRD). The etchant is developer AZ 351B diluted in DIW, a solution commonly used in photolithography. The results show a difference in the etch rates between different plasma times; AlN film grown thermally is etched 1,9 nm/s whereas the etch rate of a film with a 15 s plasma exposure time is 0,9 nm/s and 0,6 nm/s with a film with a total 35 s plasma exposure time per cycle. This result is in accordance with previous study on the influence of plasma exposure time during growth of ALD film [6]. The decrease in the wet etch rate can also be predicted from the XRD scan, as the crystallinity is enhanced by the applied plasma time; the thermal sample is amorphous, and the crystallinity is enhanced by extended plasma exposure time.

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AF10-12 ALD of TiO2 using a Titanium Precursor with a Linked Amido-cyclopentadienyl Ligand: A Density Functional Theory Study*, Romel Hidayat,* *H. Kim, Y. Choi,* Sejong University, Korea (Republic of)*; J. Seok, J. Park,* Hansol Chemical, Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

Titanium oxide (TiO_2) has been an attractive material with interest for various applications, including photocatalysts, optical coatings, and the high-permittivity dielectrics of DRAM capacitors. The atomic layer deposition (ALD) technique is used to deposit thin films with excellent step coverage, accurate thickness control, and excellent film quality. One of the most common precursors for the ALD of TiO_2 was tetrakis(dimethylamido) titanium (TDMAT). However, TDMAT showed low ALD temperatures because of its insufficient thermal stability. In general, the higher the deposition temperature, the better the physical and electrical properties of the dielectric film. Therefore, we need a Ti precursor with excellent thermal stability and reasonable reactivity to increase the ALD temperature. Thermal stability of the Ti precursor can be improved by introducing a cyclopentadienyl (C_5H_5, Cp) ligand, and tris(dimethylamido)cyclopentadienyl titanium ($CpTi(NMe_2)_3$) is more thermally stable than TDMAT [1]. We reported a Ti precursor, (2-(N-methylamido)1-methyl(ethyl-cyclopentadienyl))bis(dimethylamido) titanium (CMENT), designed to further improve the thermal stability of $CpTi(NMe_2)_3$ by linking a Cp ligand to an amido ligand [2]. In this study, we compared CMENT and $CpTi(NMe_2)_3$ by deposition experiments and density functional theory (DFT) calculations. CMENT showed higher ALD TiO_2 process temperature than $CpTi(NMe_2)_3$. The DFT simulation of thermolysis and hydrolysis of Ti precursors confirmed the better thermal stability and reactivity with hydroxyl groups of CMENT. The chemisorption of Ti precursors on a hydroxylated TiO_2 surface was also simulated. For CMENT, the linked ligand may remain on the surface after chemisorption. In contrast, after chemisorption of $CpTi(NMe_2)_3$, only a fraction of Cp would remain on the surface. Therefore, the introduction of a linked ligand enables the ALD process at higher temperatures compared to the introduction of a Cp ligand.

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AF10-13 Atomic Layer Deposition of Silicon Oxide Using a Silylamine Precursor and Ozone*, Heeju Son*, *Y. Choi, H. Han, H. Roh, Y. Kim, W. Lee,* Sejong University, Korea (Republic of)

To overcome the scaling limit of planar semiconductor devices, three-dimensional structures have been introduced, and new process technologies have been applied. The method of forming silicon oxide (SiO_2) thin film has been shifting from the conventional chemical vapor deposition (CVD) methods to atomic layer deposition (ALD) technologies for excellent step coverage and film characteristics at low process temperatures. Various silicon compounds have been studied as the precursor for the ALD of SiO_2, and the reported Si precursors can be categorized into chlorides and aminosilanes. Chloride precursors exhibit good film properties, but their low reactivity requires a large supply. Aminosilanes are more reactive than chlorides, but they have poor thermal stability and low growth rates. Silylamine compounds were investigated as the silicon precursor for the ALD of silicon nitride thin films, and superior film properties and step coverage were reported compared to aminosilane [1]. However, the study on the ALD SiO_2 using silylamine compounds was rare. In the present work, we studied the ALD SiO_2 using a silylamine compound, bis(dimethylaminomethylsilyl) trimethylsilyl amine (DTDN2-H2), as the silicon precursor. Ozone was used as the co-reactant. The maximum ALD temperature was 400°C and the growth rate of the thin film was 1.34Å/cycle at 400°C. The ALD SiO_2 films were stoichiometric pure SiO_2 and showed excellent step coverage. Raising the process temperature to 450°C improved the insulating properties of the deposited film but worsen the step coverage. The silylamine precursor could perform the ALD process with less supply at lower process temperatures than the chloride precursor. It also showed a higher growth thickness per cycle than the aminosilane precursor. We simulated the dissociative chemisorption of DTDN2-H2 on an OH-terminated SiO_2 surface by density functional theory (DFT) calculation. Surface species formed by the chemisorption may contain three silicon atoms or one silicon atom, resulting in a higher growth rate than aminosilane precursors.

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AF10-14 Reaction Mechanism and Film Characteristics of High-temperature ALD of Silicon Nitride*, Tanzia Chowdhury*, *H. Han, K. Jainuri, H. Son,* Sejong University, Korea (Republic of)*; J. Han, Y. Kim, J. Seok, J. Park,* Hansol Chemical, Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

In modern semiconductor devices, silicon nitride is an essential dielectric material that has been utilized as gate spacers, etch stop layers, and diffusion barriers. Recently, it has been applied to the charge trapping layer and the sacrificial layers in three-dimensional vertical NAND flash memory devices. Atomic layer deposition (ALD) is required to deposit silicon nitride thin films with excellent conformality in high-aspect-ratio three-dimensional patterns. There have been several reports on silicon nitride ALD processes including both thermal and plasma-assisted schemes. As the deposition temperature increased, the physical and electrical properties of the deposited thin films were improved. However, thermal decomposition occurs above a certain temperature, resulting in poor thin film properties and step coverage [1]. To date, the maximum temperatures of the genuine ALD mode have been reported to be approximately 450–500°C, and ALD processes at higher temperatures have not been reported. In the present study, we investigated the high-temperature ALD of silicon nitride using thermally stable silicon precursors. Various silicon compounds were compared using NH_3 as the co-reactant. The reaction mechanism and the film characteristics were studied. The electrical characteristics of the films, such as leakage current, breakdown voltage, dielectric constant, and oxide trapped charge densities, were determined by I-V and C-V measurements. To study the ALD reaction mechanism, the chemisorption of the precursors on an NH_2/NH-terminated silicon nitride surface was modeled and simulated by density functional theory (DFT). The possible reaction pathways for each silicon precursor were compared to explain the properties of the deposited films using different silicon precursors.

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AF10-15 Atomic Layer Deposition of Nanometer Thick Tungsten Nitride Using Anhydrous Hydrazine for Potential X-Ray Optics Application*, Dan N. Le*, *A. Kondusamy, S. Hwang, A. Ravichandran, J. Mohan, Y. Jung,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; M. Markevitch,* NASA Goddard Space Flight Center*; J. Kim,* University of Texas at Dallas

In this study, we establish a low-temperature atomic layer deposition process of high-quality ultrathin WN_x films for applications like barrier layers of Cu metallization and X-Ray mirrors. Hydrazine has been extensively investigated as a nitrogen source at low temperature in place of conventionally used ammonia, due to its high reactivity.[1] Hydrazine along with Bis(tebutylimino)bis-(dimethylamino)tungsten (VI) (BTBMW) is investigated for thermal ALD of tungsten nitride. We confirm that high quality WN_x films, with a nano-crystalline structure, can be deposited at the low temperature window.

A home-built ALD chamber was employed to deposit WN_x films at a temperature range of 250–350°C. Deposited films are analyzed by using an ellipsometer, atomic force microscopy, X-Ray diffraction spectroscopy, X-Ray reflectivity spectroscopy, and cross-sectional transmission electron microscopy.

The GPC of the deposited WN_x films saturates with a short exposure time of hydrazine (0.1s). A GPC of 0.1 nm/cycle is observed at a temperature of 300°C, which is higher than the reported growth rate of WN_x films using NH_3 at the same temperature.[2] The AFM images demonstrate a smooth surface roughness (~0.23 nm) of films deposited in the temperature range of 250–350°C. XRR determines that film density is as high as 13.0 g/cm^3. An earlier report shows films deposited using NH_3 exhibit crystalline phase after a 30-minute annealing process at 700°C.[2] Interestingly, XRD measurements of films grown with hydrazine display crystallinity with highest intensity peak at 2θ value of 37.6°. It is suspected that, at low temperature, N_2H_4 provides an ideal condition for random distributed nucleation events to occur on the surface of the amorphous region per ALD cycle.[3] ALD cycles continue to add mass to the nuclei after the formation of a nucleus allowing crystallite to grow.[3] The resistivity of the deposited films ranges between 1.34x104–2.38x10^4 µΩ.cm. Based on the results of above, a stacking structure of WN_x and one other metal nitride thin film (WN_x and AlN_x) is deposited on a SiO_2 substrate. Such an alternating stack of nitride films with different densities could be applied as X-Ray mirrors. The experiment details and results will be presented.

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AF10-16 First-Principles Investigation of Atomic Layer Deposition of Silicon Nitride Using NH_3 Plasma*, Tsung-Hsuan Yang*, *G. Hwang,* University of Texas at Austin*; P. Ventzek, T. Iwao , K. Ishibashi ,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for controlled growth of silicon nitride (SiN) thin films. The benefits of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures (<400°C). In this work, we focus on the mechanisms underlying the nitridation of Si-rich SiN surfaces with NH, NH_2, and H radicals generated from the NH_3 plasma. The surface reaction mechanisms have been examined using first-principles calculations based on density functional theory (DFT). Surface nitridation tends to proceed through the reaction of NH and NH_2 radicals with H-terminated Si-rich surfaces, leading to the formation of primary amines (Si-NH_2). H radicals are found to predominantly react with primary amines, if available, to form Si-NH_3 moieties; the NH_3 is likely to desorb from the surface rendering a Si dangling bond. It is also likely that H radicals abstract H from Si:H surface moieties creating Si dangling bonds. The Si dangling bond is predicted to be rather unreactive with both NH_3

and H_2 molecules. As such, the extent of nitridation appears to be a strong function of the flux ratio of H to NH/NH_2. The Si-N bond strength in Si-NH_2 is also found to be sensitive to the amine coverage, which in turn helps to achieve self-saturated nitridation reactions. The rate-determining steps in the nitridation process turn out to be bridging reactions (*i.e.*, Si-NH_2 + Si-NH_2–> Si-NH-Si + NH_3 or Si-H + Si-NH_2–> Si-NH-Si + H_2) depending on the primary amine coverage. Our work also predicts that the kinetics of the nitridation reactions is significantly affected by the amine surface coverage. Based on the calculation results, we will also discuss how the radical-surface chemistry would determine the deposition kinetics and the film quality.

AF10-19 Low Temperature ALD of Antimony Oxide*, J. Yang,* Leibniz Institute for Solid State and Materials Research, Germany*; S. He,* leibniz Institute for Solid State and Materials Research Dresden, Germany*; S. Lehmnann, **Amin Bahrami**, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

Antimony oxide thin films can be used as etch stop layers, dopant source for ultra-shallow doping of silicon, as anode in various batteries, fire- and flame-retardant materials, etc. In this study we report the atomic layer deposition of Sb_xO_y coatings using $SbCl_5$, $Sb(NMe_2)_3$ as antimony reactants and H_2O and H_2O_2 as an oxidizer at low temperatures. Homogenous antimony oxide deposition can be achieved on flat silicon wafers. $SbCl_5$ can react with both oxidizers, while no deposition was found using $Sb(NMe_2)_3$ and H_2O. Uniform deposition growth was found at 80 °C deposition temperature for all the systems. X-ray photoelectron spectroscopy results confirm formation of Sb_2O_3 as the main phase with some minority of Sb_2O_5 phase. The ratio of Sb_2O_3 to Sb_2O_5 is affected by the type of precursor and deposition temperature.

AF10-22 Development of Fast Response Flow Controlled Vapour Delivery System for ALD/ALE Applications*, **Krunal Girase**,* HORIBA STEC, Co., Ltd., Japan*; H. Nishizato,* HORIBA STEC, Co., Ltd. , Japan*; T. Hayashi, M. Hotta,* HORIBA STEC, Co., Ltd., Japan*; P. Lowery P.E.,* HORIBA Reno Technology Centre*; P. Totten,* HORIBA Instruments Incorporated*; T. Hoke,* HORIBA Reno Technology Centre*; T. Freeman,* HORIBA Instruments Incorporated, Poland

Atomic layer processes, such as atomic layer deposition (ALD), atomic layer etch (ALE), and selective deposition/etch processes are becoming some of the predominant methods used to achieve new device geometry shrinks with smaller lithographic nodes. The chemical vapors used in ALD processes have to be delivered at a constant concentration per pulse. In the present study, a fast response flow-controlled vapor delivery system using a piezoelectric actuated electromechanical valve was developed and implemented for ALD application. This valve shows a response time of < 1 ms for ON/OFF pulsing and < 10 ms for flow control with the ability of programable waveform control. Due to fast flow control, this system reduces the waste of precursor by eliminating vent lines and increase the repeatability of vapor delivery per pulse. Both methods of vaporization: vapor drawer and bubbling method were demonstrated for vapor delivery to the ALD reactor and the results were found repeatable pulse to pulse. For the bubbling method of vaporization, an auto pressure regulator was used to control carrier gas pressure and hence to control the concentration of precursor vapor. A new self-contained, closed-loop design is being developed with piezoelectric-drive and an intuitive UI that will allow the end-user to be able to control variable pulse cycle for ALD/ALE applications.

AF10-25 Thermal Atomic Layer Deposition of Elemental Antimony at Room Temperature: Growth and Uniformity Studies*, **Majeda Al Hareri**, D. Emslie,* McMaster University, Canada

As feature sizes on devices continue to decrease, atomic layer deposition has become an invaluable tool for the fabrication of highly uniform and conformal thin films with nano-scale control of film thickness. Additionally, the utilization of low temperature thermal ALD techniques can aid in obtaining continuous films of low-melting metallic films that often observe issues with film continuity at low thicknesses as a result of agglomeration.[1,2] In 2011, the first elemental non-metal thermal ALD process was reported, which involved the use of tris(triethylsilyl)antimony ($Sb(SiEt_3)_3$) and antimony trichloride ($SbCl_3$) to produce thin films of elemental antimony through novel dehalosilylation surface chemistry.[3] Due to the fact that antimony has a low melting point, and is a common component in various micro- and nanomaterials,[4,5] reduction of the deposition temperature in this process may prove beneficial as a means to improve nucleation and prevent agglomeration.

Switching to the smaller and more volatile methyl derivative, $Sb(SiMe_3)_3$, allowed for a substantial decrease in the precursor delivery and deposition temperatures, as well as an improvement in nucleation on H-terminated silicon and SiO_2. We present the first report of room temperature thermal ALD of a pure element, and an investigation of the effects of substrate temperature and pulse durations on the uniformity of the deposited films at low thicknesses (< 10 nm).

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AF10-28 Impact of Different Intermediate Layers on the Morphology and Crystallinity of TiO_2 Grown on Carbon Nanotubes by Atomic Layer Deposition*, **Jiao Wang**, Z. Yin, E. List-Kratochvil, N. Pinna,* Humboldt-Universität zu Berlin, Germany

Nanocomposites of TiO_2 and carbon nanotubes (CNTs) have been extensively studied in photocatalysis, electrochemical sensing and energy storage over the last decade. The unique properties of these nanocomposites are greatly dependent on the morphology, crystallinity and homogeneity of the TiO_2 films. However, a fine control of the film microstructure is still challenging due to a lack of understanding of the early stages of the TiO_2 growth. The presence of an intermediate buffer layer can cause remarkable changes in the morphological and structural properties of the coatings. Here, TiO_2 films deposited by atomic layer deposition (ALD) on CNTs without and with different intermediate layers (Al_2O_3 and ZnO) have been systematically investigated. Compared to bare CNTs, it is suggested that these two intermediate layers with higher surface energy can lead to a delay of the TiO_2 crystallization, ultimately leading to the growth of conformal crystalline TiO_2 films. This study demonstrates a strategy to tailor the microstructure and the properties of thin-films via ALD by applying intermediate layers, and provides information about the role of surface energy of the substrate on crystallization and growth behavior of ALD thin films.

AF10-31 *Growth, Intermixing and Composition Control of Atomic Layer Deposited Zinc Tin Oxide* *, **Poorani Gnanasambandan**, R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Zinc tin oxide being abundant and non-toxic has varied applications from gas sensors, thin film transistors, to window and buffer layers in thin film solar cells, etc. The synthesis of zinc tin oxide (ZTO) by atomic layer deposition (ALD) has been widely studied with different Sn precursors and reactants [1][2]. Atomic layer deposition of ternary materials by mixing two binary ALD processes has its challenges [3]; the composition and growth rates of ternary materials deviate from that of the binary processes due to various factors, including the interaction between different precursors.

Previous studies aimed to understand deeper the ZTO ALD processes, by investigating the underlying surface chemistry of the precursors, influence of substrate temperature and constructing analytical models from observed deviations in the growth rate [4][5][6]. Still there remains a need for a consistent model that explains the nonidealities observed in the growth of ZTO by ALD under various processing conditions.

We study atomic layer deposited $Zn_{1-x}Sn_xO$ with x varying from 0.1 to 0.4 by optimizing the growth conditions with varying deposition temperatures and supercycle parameters such as pulse ratios and bilayer period. We analyze the deviation of growth rate and composition of ZTO from the respective binary ALD processes. We find that the composition of [Sn]/([Sn]+[Sn]) has a strong dependence on the deposition temperature in contradiction to Ref. [6]. We aim to achieve precise control over the composition and demonstrate the effect of doping on the band alignment, electrical and optical properties.

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AF10-34 Hollow Cathode Plasma Enhanced Atomic Layer Deposition of Vanadium Oxide Films: *in situ* Ellipsometric Monitoring of Film Growth with TEMAV and Oxygen Plasma*, Adnan Mohammad*, *K. Joshi, S. Ilhom, . Shukla, B. Willis, B. Wells,* Uconn*; A. Okyay,* Stanford University*; N. Biyikli,* Uconn

Vanadium dioxide is a bistate phase-change material that shows a low temperature phase transition from monoclinic to tetragonal rutile structure. The transition is called MIT (metal-insulator transition) which can be used in electrical and optical switching applications.There are several reports in the literature showing thermal atomic layer deposition (ALD) of vanadium oxide with TEMAV and VTIP precursors and water or ozone as co-reactant. The reported as-grown vanadium oxide films are mostly amorphous, which are typically annealed at high substrate temperatures (> 600 ℃) to achieve crystalline films. However, no significant report is yet found on VOx films grown by plasma ALD, where O2 plasma is used as the coreactant.

In this work we report on the low-temperature crystalline VOx deposition in a hollow cathode plasma reactor featuring in situ ellipsomteric monitoring, in which we utilized TEMAV and O2 plasma as the metal precursor and co-reactant, respectively. The parameters used for the plasma ALD experiments are 0.1 s of TEMAV pulse with 10 sccm of N2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O2 plasma for 10 s, plasma power 50W-300W and finally another 10 s of Ar purge. In addition, the TEMAV precursor cylinder and line is heated at 110 °C to provide sufficient amount of precursor vapor into the growth chamber. We found a maximum growth per cycle (GPC) of 1.1 Å from in situ ellipsometry measurements. The x-ray diffraction (XRD) measurements revealed crystalline V2O5 phase for the as-deposited films and the ex situ ellipsometry showed a refractive index of 2.45. The next step is to anneal the as-grown films to achieve VO2 and to do temperature-dependent electrical and structural characterization of the VO2 samples to confirm the MIT character of the films.

AF10-37 Combined Fabrication and Testing System for Atomic Layer Deposition Microchannel Plates*, Anil Mane*, *J. Elam,* Argonne National Laboratory, USA

Microchannel plates (MCPs) are two dimensional solid-state electron multipliers consisting of a thin plate permeated with millions of parallel, micron-scale, high aspect ratio pores.Each pore acts independently to amplify electron signals incident on the front surface allowing MCPs to be utilized in imaging detectors for astronomy, high-energy physics, medical imaging (PET scanner), homeland security and the military (night vision devices).Over the last decade, we have researched and developed MCPs fabricated by depositing ALD nanostructured coatings on high aspect ratio (40-100), high porosity (>65%) glass microcapillary array (MCA) substrates. These ALD MCPs have many advantages over MCPs manufactured by conventional methods.This experience taught us that achieving uniform, precise coatings on these complex MCA substrates is challenging and time consuming. To streamline ALD MCP process development and to enable systematic studies of MCP structure and function, we constructed an integrated system which combines a viscous flow ALD reactor for coating high aspect ratio MCA substrates with a sample transfer chamber and high voltage MCP testing chamber, both of which are maintained under high vacuum. This combined system allows us to measure critical MCP metrics, such as gain and pulse height distribution, after each ALD precursor exposure to map out the MCP performance as a function of the ALD film thickness and composition.Critically, these measurements are performed without exposing the MCP to air which avoids the inadvertent formation of surface hydroxides, carbonates and other contaminants that can alter the materials properties such as the secondary electron emission (SEE) of the MCP surface.To our knowledge, this is the first integrated system combining ALD MCP fabrication and testing.Our initial tests used 33mm diameter borosilicate glass MCAs (Incom, Inc.) as MCP substrates that we first functionalized using an ALD nanocomposite tunable resistive coating.Next, we performed Al_2O_3 ALD using trimethyl aluminum and H_2O to deposit the SEE layer and measured the current-voltage characteristics as a function of the ALD Al_2O_3 film thickness. We used these measurements to extract the gain and SEE values which agree with previous measurements for ALD Al_2O_3 thin films. We believe this new system will reduce ALD MCP process development times by a factor of 10 and may be suitable for ALD process development in vertical interconnect access (VIA) substrates (e.g. TSV, TGV and TPV) for vertically integrated semiconductor microelectronics devices.

ALD Fundamentals
Room On Demand - Session AF2
Precursors and Chemistry: Simulation, Modeling, and Theory of ALD

AF2-1 Comparison of ALD Saturation Profiles Simulated With Two Theoretical Models*, Jihong Yim*, *E. Verkama, R. L. Puurunen,* Aalto University, Finland

Self-terminating chemistry of atomic layer deposition (ALD) process enables one to grow pinhole free conformal thin films on high-aspect-ratio (HAR) structures. ALD has attracted ever more attention in diverse applications, such as microelectronics and nanostructured catalyst preparation.[1] Yet, it is essential to optimize ALD process parameters for the conformal deposition especially on HARs. Our previous study investigated the effect of experimental parameters on conformality using saturation profiles of archetypical trimethylaluminum-water ALD processes in lateral HARs with an aspect ratio of typically 10000:1.[2]

The investigation on the effect of process parameters on ALD conformality is continued by simulating ALD saturation profiles with two modeling approaches: a MATLAB simulation based on a diffusion–reaction modeling (Model A)[3,4] and a Python simulation based on a ballistic transport modelling (Model B).[5,6] These simulated saturation profiles are compared to each other in approximately the same condition. While the main features of the simulated saturation profiles are similar, differences are found in the value of 50% thickness penetration depth ($PD_{50\%}$) and slope at $PD_{50\%}$, as well as the shape of the tail region.

Sticking coefficient of ALD reactants describes ALD growth kinetics. A recent study by Arts et al.[7] reported a method to back-extract the sticking coefficient value from the slope of saturation profile. By using this method, we back-extract the sticking coefficient values from the saturation profiles simulated by Models A and B and compare those values to the ones initially set for running the simulations. Interestingly, for both Models A and B, the sticking coefficient values set for the simulations differ somewhat from the ones back-extracted.

Acknowledgement

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AF2-2 Theoretical Prediction of the Adverse Effects of H^+/Cl^- Byproducts on SiN Atomic Layer Deposition with Dichlorosilane*, **Tsung-Hsuan Yang,** G. Hwang, E. Cheng,* University of Texas at Austin*; P. Ventzek, T. Iwao , K. Ishibashi ,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for controlled growth of silicon nitride (SiN) thin films. The advantages of PEALD may include excellent conformality, precise thickness control, and high quality at relatively low temperatures. In this talk, we will present molecular mechanisms underlying the PEALD of SiN thin films using dichlorosilane (DCS) as the Si source and N_2/NH_3 plasma as the N source. The adsorption and decomposition of DCS have been found to be sensitive to the surface functional groups; especially, the presence of primary amines plays a critical role in the silicon deposition half cycle. According to our recent studies, the byproducts of DCS decomposition, $H^{\delta+}/Cl^{\delta-}$ pairs, may have a significant effect on the film quality and deposition temperature. First-principles calculations predict that $H^{\delta+}/Cl^{\delta-}$ pairs are strongly bound to the H-terminated N-rich surface by forming $–NH_3^+/Cl^-$ ionic complexes. Because of the sizable binding energy (~ 1 eV), it would be difficult to remove $H^{\delta+}/Cl^{\delta-}$ pairs from the surface unless the PEALD temperature is substantially high. This implies that the reaction of DCS with surface primary amines, and in turn SiN ALD, can be significantly suppressed by the presence of $H^{\delta+}/Cl^{\delta-}$ pairs at relatively low temperatures, which has been confirmed by very recent FTIR measurements at 200 °C. In this talk, we will also discuss a potential method to effectively remove $H^{\delta+}/Cl^{\delta-}$ pairs at low temperatures.

ALD Fundamentals
Room On Demand - Session AF3
Precursors and Chemistry: Mechanisms

AF3-1 Titanium Nitride ALD Process Using High Purity Hydrazine: N_2H_4 Reactivity in Gas Phase*, **Hayato Murata,** H. Shimizu, K. Andachi,* TAIYO NIPPON SANSO Corporation, Japan*; D. Alvarez , J. Spiegelman,* RASIRC*; K. Suzuki,* TAIYO NIPPON SANSO Corporation, Japan

ALD titanium nitride (TiN) with lower resistivity has attracted an attention as DRAM device has higer-aspect-ratio capacitors with its scaling. We reported that ALD TiN films using $TiCl_4$ and hydrazine (Hy, N_2H_4) has higher GPC, smaller roughness, less chlorine (Cl) impurities, and lower resistivity [1]. Here, we delivered N_2H_4 employing BRUTE Hydrazine (RASIRC, Inc.) which enabled safe delivery of high-purity N_2H_4 gas[2]. In addition to safety and quality of N_2H_4, lab-to-fab scale-up could be efficiently achieved through understanding reaction mechanism of N_2H_4 in the ALD process. In this study, we investigated gas-phase reaction of N_2H_4 in the ALD process and an effect of gas-phase reaction on GPC (growth per cycle).

First, N_2H_4 decomposition was observed above 200°C at 133Pa by quadruple mass spectrometry installed at downstream of a hot-wall tubular reactor. When a gas mixture of 10 sccm N_2H_4 and 240 sccm N_2 flowed through the reactor at 300°C and 400°C (380 cm/s and 450 cm/s), 38% and 55% of N_2H_4 were respectively decomposed before reaching to a substrate (35 cm heated zone before the substrate). Thus, lower-concentration hydrazine is delivered to the substrate in ALD process at higher temperature.

Next, TiN ALD process using $TiCl_4/N_2H_4$ was performed at 250-400°C. GPCs in $TiCl_4/N_2H_4$ ALD were found to be 0.42-0.32 Å/cycle while those in $TiCl_4/NH_3$ ALD were 0.10-0.27 Å/cycle at 250-400°C. Interestingly, the GPC in $TiCl_4/N_2H_4$ ALD was lower at higher temperature, correlating to the hydrazine concentration estimated by the decomposition study. Further enhancement in throughput could be available by preventing the decomposition of N_2H_4 before reaching to the substrate.

In addition, ALD TiN film using $TiCl_4/N_2H_4$ likely had as good quality as sputtered TiN. Refractive index (R.I.) of $TiCl_4/N_2H_4$ film was about 1.68-1.73 at 250-300°C while R.I. of typical sputtered TiN was about 1.66. In contrast, R.I. of $TiCl_4/NH_3$ film formed at 250-300°C was larger than 2.00 likely due to the formation of titanium oxide whose R.I. is 2.4-2.5. The R.I. results indicate probably that higher-concentration hydrazine have an effect on TiN film quality at lower temperature.

Thus, since TiN ALD using $TiCl_4/N_2H_4$ has various advantages over that using $TiCl_4/NH_3$, N_2H_4 is expected to improve both throughput of ALD and quality of nitride ALD films.

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AF3-2 Mechanistic Insights into the Thermal ALD of Gold: Infrared, Mass Balance, Nucleation, and Epitaxy*, P. Liu,* Argonne National Laboratory*; A. Hock,* Illinois Institute of Technology*; **Alex Martinson,*** Argonne National Laboratory

An *in situ* microbalance and infrared spectroscopic study of alternating exposures to $Me_2Au(S_2CNEt_2)$ and ozone illuminates the organometallic chemistry that allows for the thermal atomic layer deposition (ALD) of gold. The synthetic yield of $Me_2Au(S_2CNEt_2)$ was also improved but remains well below 50%, leaving a significant room for improvement of the synthetic method and further motivating the search for related precursors. When we apply deposition conditions optimized for Au ALD growth on itself to oxide substrates the result is a long (300+ cycle) nucleation period, similar to other noble metal ALD processes. After steady-state growth is achieved, the final growth rate (0.14 nm/cycle) is measured to be significantly greater than previously estimated. *In situ* infrared spectroscopy informed by first-principles computation provides insight into the surface chemistry of the self-limiting half-reactions, which are consistent with an oxidized Au surface mechanism. The diethyldithiocarbamate ligand, or remnants thereof, is removed and volatilized by ozone, which is also required for activation of the growing Au surface to endow sufficient activity for reaction with the next Au precursor exposure. This reactivity is significantly reduced, even after ligand removal, upon exposure to a reducing CO atmosphere. X-ray diffraction of ALD-grown gold on silicon, silica, sapphire, and mica reveals consistent out-of-plane oriented crystalline film growth as well as epitaxially directed in-plane orientation on closely lattice-matched mica at a relatively low growth temperature of 180 °C. A more complete understanding of ALD gold nucleation, surface chemistry, and epitaxy will inform the next generation of low-temperature, nanoscale, textured depositions that are applicable to high surface area supports.

AF3-3 Oxygen Reservoirs in Metal Oxides: Mechanisms of Reactive Species Formation and Transport in Atomic Layer Deposition of Fe_2O_3 and NiO*, **Joel Schneider**, C. de Paula, N. Richey, J. Baker, S. Bent,* Stanford University

The ability of atomic layer deposition (ALD) to deposit materials in a uniform, conformal, and controlled fashion hinges on the surface reactions being self-limiting. While this is often the case, not every ALD process is so well-behaved, and understanding and controlling growth mechanisms are critical given the increasing material demands of ALD. Previous work has shown that the ALD reactions of iron (III) oxide are not limited to the substrate surface but rather involve sub-surface mechanisms. This work uses *in situ* techniques to investigate these mechanisms of ALD growth and the role of active species transport through the film, using ozone-based ALD of Fe_2O_3 and NiO as comparative case studies.

Iron and nickel oxide thin films were deposited using metallocene precursors with ozone, and film thickness was monitored using ellipsometry. *Ex situ* angle-resolved X-ray photoelectron spectroscopy (XPS) and grazing-incidence wide-angle X-ray scattering (GIWAXS) revealed subsurface changes and in some cases the formation of a layer of superstoichiometric oxygen near the film surface that correlates with O_3 exposure. Quartz crystal microbalance and *in vacuo* XPS were then employed to probe the sub-surface storage of superstoichiometric oxygen. Oxygen is present in two different chemical states within Fe_2O_3, and it was found the introduction of superstoichiometric oxygen with O_3 and its consumption by TBF track most strongly with the lower binding energy state of oxygen. Comparisons to the behavior of the NiO process were also made, and through *in situ* quadrupole mass spectrometry to examine gaseous reaction byproducts, stored oxygen is observed to be in a reactive form that actively participates in ALD half-reactions.

The storage and transport of oxygen through the film was also investigated. GIWAXS measurements show sub-surface transport of oxygen correlates with the reorientation of the crystalline domains such that the lattice axis with most facile oxygen diffusion preferentially orients parallel to the direction of oxygen transport. Trends regarding the degree of crystallinity and domain orientation were also observed. These studies shed light on the fundamental chemical mechanisms behind reactive oxygen species in metal oxide ALD, with additional work suggesting these mechanisms can be leveraged in enhancing growth in both ternary ALD and catalytically activated ALD, posing implications for the broader class of ozone- and oxygen plasma-based ALD processes.

AF3-4 Nonaqueous Atomic Layer Deposition of Zinc Oxide Using Diethylzinc and Ethanol*, Miso Kim, E. Shin, J. Hwang, B. Shong,* Hongik University, Korea (Republic of)

Zinc oxide (ZnO) is a transparent wide-band gap semiconductor that can be used in various fields such as thin film transistors (TFTs), gas sensors, and catalysts. Atomic layer deposition (ALD) of ZnO is widely applied due to the ability to form conformal high-quality thin films at the Angstrom level. Most previous studies on ZnO ALD utilized a few well-known precursors and reactants such as diethylzinc (DEZ), dimethylzinc (DMZ), H_2O and O_3. However, O_3 and H_2O oxidants have relatively strong reactivity, so that they are not suitable for substrates that are easily oxidized or reactive with water. Therefore, development of nonaqueous alternative ALD process for ZnO is desired. In this study, we introduce ALD of ZnO using ethanol as a nonaqueous oxidant. Density functional theory (DFT) results indicated that the β-H of the ethanol molecule is crucial in the reaction mechanism for removal of C moieties during the oxidant pulse. Using DEZ as Zn precursor, a typical ALD growth behavior and highly conformal films of ZnO were obtained between 100-300 °C. Compared to the ALD ZnO films deposited with H_2O, nonaqueous-ALD ZnO films showed similar C content, lower crystallinity, higher conductivity, and higher mobility.

ALD Fundamentals
Room On Demand - Session AF4
Growth and Characterization: Surface Science of ALD

AF4-1 Atomic Layer Deposition of Bimetallic Alloy and Work Function Modulation Using Discrete Feeding Method*, Ji Won Han, Y. Kim, J. Heo, T. Park,* Hanyang University, Korea

For the continuous scaling of semiconductor based nano-electronics, complementary metal oxide semiconductor (CMOS) field effect transistor (FET) also need to be scaled. 3D structures, such as FinFET, have been applied to suppress the short channel effect, and gate all around (GAA) structure which has all four side of channel is surrounded by the gate metal is anticipated as the next generation device structure. Atomic layer deposition (ALD) have been used as deposition technique since deposition of uniform and conformal film on complicated structure is essential and ALD is only way to successfully accomplish the requirements. Also, workfunction materials for both pMOS and nMOS are needed to developed. However, metals having a low work function suitable for nMOS have poor oxidation resistance and thermal stability due to low oxide formation energy. To overcome the limitation, ALD-based metal nitride and metal carbide are being studied as an alternative, but recent researches are still unsatisfactory.

In this work, we demonstrated deposition of bimetallic alloy film of n-type metal and p-type metal *via* ALD, and modulation of the ratio using discrete feeding method (DFM). DFM is an advanced ALD process that improves reaction efficiency, deposition behavior and overall properties of film by removing physisorbed precursors with cut-in purge introduced between subdivided precursor feeding.

It was confirmed that ratio of n-type metal in the film was able to be controlled in the range of 30~50 %, and detailed mechanism of composition modulation through DFM was elucidated based on change of deposition behavior. Resistivity of bimetallic alloy film was applicable to CMOS regardless of the process variation, while slightly changed depending on its composition. Also, effective workfunction of the film was decreased as ratio of n type metal increased, and since the effect from microstructure of the film is added, bimetallic alloy film having workfunction of 4.1 eV that is identical to conduction band minimum of Si was obtained.

AF4-2 Novel ALD Study of TiO_2 and ZrO_2 on Pmma Substrates as Separate and Mixed Oxide Thin Films for Enhanced Biomaterial Functionalization*, Mina Shahmohammadi,* University of Illinois - Chicago*; B. Nagay, V. Barão,* University of Campinas (UNICAMP), Brazil*; C. Sukotjo, C. Takoudis,* University of Illinois - Chicago

Titanium(IV) oxide (TiO_2) and zirconium oxide (ZrO_2) are well-known materials due to their biocompatibility, hydrophilicity, antimicrobial activity, excellent corrosion resistance, and low cost. Polymethyl methacrylate (PMMA), on the other hand, is a promising polymer with a huge range of applications such as denture base materials. However, its poor surface properties lead to fracture and deformation.The mainline inquiry that is to be explored through this work is how functionalization of PMMA surface would make this polymer more stable and robust in the aggressive oral environment and reduce biofilm formation when used in dental applications. Here, low-temperature Atomic Layer Deposition (ALD) was used to systematically deposit TiO_2 and ZrO_2 as separate and mixed oxide thin films on PMMA substrates. Five groups are deposited and characterized: 1. Non-deposited PMMA (control); 2. TiO_2 deposited PMMA; 3. ZrO_2 deposited PMMA; 4. Mixed TiO_2 and ZrO_2 film with 1:1 thickness ratio of TiO_2:ZrO_2 (TZO1); 5. Mixed TiO_2 and ZrO_2 film with 3:1 thickness ratio of TiO_2:ZrO_2 (TZO3). Tetrakis(dimethylamido)titanium (TDMAT) and tetrakis(dimethylamido)zirconium (TDMAZ) precursors were used to deposit TiO_2 and ZrO_2 thin films, respectively and ozone was used as the oxidizer. The reactor temperature for all the depositions was kept at 120ºC and the precursor bubblers of TDMAT and TDMAZ were both kept at 70ºC. Spectroscopic ellipsometry was used to measure the metal oxide film thickness on PMMA substrates. The wettability, composition, and surface roughness of each group were examined with water contact angle measurements, x-ray photoelectron spectroscopy (XPS), and Atomic Force Microscopy (AFM), respectively. A systematic ALD study was successfully performed on PMMA to improve its properties for dental applications. The coatings increased the wettability of PMMA surface by over 30%,which is a necessary characteristic for dental applications since a hydrophilic surface has less potential for bacterial attachment. AFM revealed not a significant change in the surface roughness of PMMA after ALD, which corroborates conformal deposition of the thin films across the substrate. XPS confirmed the presence of each oxide on the surface of PMMA for single oxide films and more importantly, the presence of both oxides for the mixture. The antibacterial activity of each group as well as the studies on the surface roughness and hardness of each group before and after thermal aging will be discussed.

AF4-3 Advanced Atomic Layer Deposition of Metal Oxide Films With Discrete Feeding Method*, Jae Chan Park,* Hanyang University, Korea*; S. Lee, S. Yoo, J. Lee, K. Dae, J. Jang,* Korea Basic Science Institute, Korea (Republic of)*; W. Kim, T. Park,* Hanyang University, Korea

HfO_2, the most widely used gate dielectric layer for semiconductor devices, was grown via atomic layer deposition with discrete feeding method (DFM), and its physical, chemical and electrical properties were studied. In a typical ALD process, all the substrate surface sites hardly react with precursor or reactant molecules, even in adsorption saturated condition, because physisorbed precursor and byproduct molecules screen the subjacent surface sites. The DFM process consists of multiple steps of feeding and purging precursor molecules prior to the reactant feeding/purging step, which can efficiently remove the physisorbed precursor molecules and byproducts.

The assorted properties of HfO_2 thin film were improved with DFM process in various ways; i) increased film density, ii) decreased thickness of the HfO_2/Si interfacial layer, and iii) decreased impurity level in the film, which are crucial for the electrical properties of the high-k dielectrics. These are associated with increased adsorption and filling efficiency of precursor molecules on the substrate surface during initial stage of ALD. The detailed experimental results will be presented.

AF4-4 Study of SiO_2 Growth Mechanism Between a Single SiO_2 and (HfO_2)/(SiO_2) Nanolaminate Formation by ALD Using TDMAS and H_2O Gas*, Toshihide Nabatame,* WPI-MANA, National Institute for Materials Science, Japan*; M. Inoue, E. Maeda, T. Onaya, M. Hirose, R. Kobayashi,* National Institute for Materials Science, Japan*; A. Ohi,* WPI-MANA, National Institute for Materials Science, Japan*; N. Ikeda,* National Institute for Materials Science, Japan*; K. Tsukagoshi,* WPI-MANA, National Institute for Materials Science, Japan

Recently, Hafnium silicate ($HfSiO_x$) material has been investigated as dielectrics for AlGaN/GaN high-electron-mobility transistors. To form $HfSiO_x$, A HfO_2 and SiO_2 (HfO_2)/(SiO_2) nanolaminate film was generally deposited by plasma-enhanced atomic layer deposition (PE-ALD) using tetrakis(dimethylamino)hafnium (TDMAHf) and tris(dimethylamino)silane (TDMAS) and O_2 plasma [1]. This is because the SiO_2 film could not deposit by ALD using TDMAS precursor and H_2O gas. The water gas supply process during ALD sequence is a key point to understand this mechanism of no SiO_2 deposition. In this paper, we study the (HfO_2)/(SiO_2) nanolaminate growth by ALD at 300°C using TDMAHf and TDMAS precursors and H_2O gas. We also discuss about SiO_2 growth mechanism based on data of a single SiO_2 and (HfO_2)/(SiO_2) nanolaminate films.

The growth per cycle (GPC) values of HfO_2 films on p-Si/SiO_2 substrate by ALD with H_2O gas and PE-ALD with O_2 plasma at 300°C using TDMAHf were 0.085 and 0.082 nm/cycle, respectively. On the other hand, the GPC value of SiO_2 film by ALD at 300°C using TDMAS and H_2O gas was ~0 nm/cycle while the GPC value by PE-ALD was 0.043 nm/cycle. Furthermore, the

$(HfO_2)/(SiO_2)$ nanolaminate film was deposited by ALD using TDMAHf and TDMAS and H_2O gas. The numbers of ALD cycles (2 and 1) used to deposit the HfO_2 and SiO_2 layers. The GPC of the $(HfO_2)/(SiO_2)$ (2/1) nanolaminate film was found to be 0.25 nm/cycle. This GPC value was closely same as that of the PE-ALD. The Hf:Si ratios in the $(HfO_2)/(SiO_2)$ nanolaminate film were estimated to be 0.59:0.41 and 0.57:0.43 by ALD and PE-ALD, respectively, based on XPS and EDS analysis. In our previous research, we found that the adsorption of the TDMAS precursor strongly depends on the difference in the electronegativities between metal and oxygen of the Metal-O underlayer [2]. Here, we discuss the SiO_2 growth mechanism by ALD using TDMAS and H_2O gas. In the $(HfO_2)/(SiO_2)$ nanolaminate deposition, the TDMAS precursors adsorb on the Hf-O and Si-O areas of the underlayer. Next, the adsorbed TDMAS on the Hf-O area easily react with H_2O gas but no reaction on Si-O area during H_2O gas supply process. This is because TDMAS precursor was partially decomposed on the Hf-O and activated. As a result, the SiO_2 film could be selectively formed on Hf-O area by the oxidation reaction between activated TDMAS precursor and H_2O gas.

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AF4-5 Discovery of Crystalline Anatase on Fluorine-Rich Carbon Substrates During Low Temperature ALD of Ultra-Thin TiO2*, **Brian Butkus, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee,* University of Central Florida

We discover crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$when deposited on a fluorine-rich carbon substrate using titanium(IV) isopropoxide (TTIP) and O2 plasma. Highly crystalline anatase phase has been detected in films deposited at temperatures as low as 100 ^oC and with thickness of only ~ 4 nm. On the other hand, TiO_2 films deposited on other forms of carbon substrates, glass and silicon, consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO_2 and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

TiO_2 was deposited on hydrophobic, polytetrafluoroethylene (PTFE) coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store) using a Veeco® Fiji Gen2 ALDsystem. ALD temperatures were varied from 100 ^oC to 200 ^oC and O_2 plasma (300 W) and H_2O were used as oxidants. Target film thickness varied from 4 nm to 22 nm. Raman, Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) were used to characterize the films. Raman spectroscopy data indicated that anatase TiO_2 was observed on all AvCarb GDS2230 substrates using O_2 plasma as an oxidant, including films as thin as 4 nm and, deposited at temperatures as low as 100 ^oC. When the oxidant is switched to H_2O, the anatase phase is still found, though significantly weaker. An interfacial layer of ALD Al_2O_3suppresses the growth of anatase phase. XPS data indicates that in films that show anatase TiO_2, Ti-F bond formation occurs at the preliminary deposition stages. This structurally differentiates the amorphous TiO_2on non-fluorinated substrates which do not show the presence of the Ti-F bond. The presence of fluorine on the surface of the carbon paper acts as a 'structure directing agent' [1-5] where the resulting flourolysis reaction between TTIP with PTFE drives the TiO_2 crystallizing into anatase film.

Fluorine doped crystallization in Ti-O systems have been reported in sol-gel and hydrothermal approaches to synthesize TiO_2 powders.[6, 7] Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO_2 films. The approach highlighted here can lead to area selective and in situ crystallization of films using suitable surface initiation chemistries.

AF4-6 Thin Films Island Structure Analysis Using X-Ray Photoelectron Spectroscopy Methodology*, V. Afanas'ev, **Daniil Selyakov,*** Moscow Power Engineering Institute, Russian Federation

Overlayer thickness determination is an important application of X-ray Photoelectron Spectroscopy (XPS). The methodology is based on measurement of substrate and film peak intensities and assumes the presence of a plane-parallel film located on a semi-infinite flat substrate. We will analyze how the XPS signal intensity changes if the film is not a flat homogeneous layer but constitute an island (cluster) structure, which may be energetically favorable for the atoms of the film. Such structures are typical of gold in submonolayer configurations. XPS spectra were measured for three samples (gold films of different thicknesses located on top of silicon substrates) at five different angles and have been interpreted by the straight line approximation model, developed within XPS framework. The effect of a decrease in the value of the effective average coating thickness (d) with a detecting angle increase was observed, when signal is interpreted within flat homogeneous layer coating model. Considering the configuration of an island surface coverage (the simplest model when the half of the silicon surface is covered with plane-parallel islands with a thickness of 2d we can compare the behavior of the theoretical curves showing the dependence of the signal intensity ratio for island and uniform coverage and see that if the flux of photoelectrons is detected at grazing angles, the curves will coincide. The value of the critical angle at which curves coincidence will be determined by the shape of the islands. The presence of an island surface coating can be confirmed by XPS measurements with an angular resolution and will be accompanied by a decrease in the layer thickness values determined by traditional XPS methodology as the detecting angles approach the grazing angle. The average value of the film thickness (the thickness of an equivalent homogeneous layer) is determined by detecting the XPS signal at angles exceeding the critical angle determined by the island morphology. The simplest model of an island coating makes it possible to qualitatively interpret the effect of a decrease of the effective average coating thickness observed in XPS experiments with an angular resolution.

AF4-9 Thermal and Plasma Enhanced Atomic Layer Deposition of Tio_2 from Amide and Alkoxide Precursors: Growth Characteristics and Photoelectrochemical Performance*, **Shane O'Donnell**, F. Jose, K. Shiel, M. Snelgrove, C. McFeely, R. O'Connor ,* Dublin City University, Ireland

Due to its low cost and suitable band edge positions, Si has been under investigation as a photoanode material for water oxidation for some time^1. However, as a result of poor stability in the oxidative environment, Si is unsuitable for extended use without a protective layer to prevent surface oxidation. Ultra-thin titanium dioxide (TiO_2) films deposited by atomic layer deposition (ALD) have been used as protective coatings and are shown to enhance Si photoanode lifetimeby distancing the oxidation reaction from the photoanode surface^2.

This study details the nucleation, growth chemistry, and photoelectrochemical performance of 2 nm TiO_2 thin films on Si prepared via atomic layer deposition (ALD). We investigate in detail the growth characteristics of films by plasma enhanced and thermal ALD using x-ray photoelectron spectroscopy (XPS), without breaking vacuum. Growth and charactersiation takes place in a custom designed system with a commercial ALD reactor (Oxford Instruments FlexAl) coupled in vacuum via fast transfer robotic handler allowing for analysis of the nucleation and growth chemistry with half-cycle resolution.

The precursors investigated in this study are titanium isopropoxide (TTIP) and Tetrakis(dimethylamido)titanium (TDMAT). Each precursor material was employed to grow TiO_2 using thermal (H_2O co-reactant) and plasma enhanced (O_2 plasma co-reactant) ALD using the manufacturer's optimised recipes, and the effect of post deposition treatments in reducing and oxidising ambients was also investigated. The photoelectrochemical performance was monitored to link the impact of precursor and co-reactant choice on surface chemistry and the measured photocurrent.

TiO_2 grown by plasma enhanced ALD results in cleaner films with reduced carbon incorporation from the precursor ligands and titanium exclusively in the 4+ oxidation state. However, despite carbon conentrations of up to 15%, thermally grown films show improved photocurrent. This increased photocurrent is correlated with presence of titanium suboxides observed in the Ti 2p peak of these films. This suggests that oxygen vacancies improve the charge transport through the films. Post deposition annealing in a H_2 ambient is shown to further improve photocurrent in all cases. Thermal annealing in atmosphere leads to even higher photocurrent, enhanced photocurrent stability, and uniform chemistry across all films

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ALD Fundamentals
Room On Demand - Session AF5

Growth and Characterization: High Aspect Ratio/High Surface Area/Powder ALD

AF5-1 Conformal Atomic Layer Deposition of Ultra-Thin Conductive Silver Films

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In the fabrication of microelectronic devices, which include DRAM capacitors, transistors, and back-end-of line (BEOL) interconnects, silver (Ag) is of particular interest due to its low electrical resistivity and low residual stress compared to Cu, and allows downscaling to less than 100 nm without a considerable increase in resistivity [1]. While the deposition of highly uniform and conformal conductive ultra-thin Ag films is of great interest due to the miniaturization and three-dimensional architecture of semiconductor devices [2,3], there is currently no reliable Ag deposition method providing conformal ultra-thin conductive films, mainly due to the island deposition mode of standard non line-of-sight deposition methods, including atomic layer deposition (ALD) [3,4].

We have investigated the conformal deposition of silver films by plasma-enhanced atomic layer deposition (PEALD) using large horizontal aspect ratio (LHAR) structures from Pillarhall®, including a new process in two steps allowing the conformal deposition of ultra-thin conductive silver films [5]. While the standard PEALD process shows an exponential decrease of the deposited material in the LHAR structure, presumably limited by the recombination of plasma radicals on the walls, our new approach demonstrates high conformality of the deposited film on complex lateral high aspect ratio structures (up to 100). Moreover the obtained layer remains continuous inside the structure.

This new processing approach opens a very promising route for the use of ultra-thin silver films for electronic and optoelectronic applications, and could be extended to other metals deposited from metal-organic precursors, in particular copper and gold, for which the deposition using chemical vapor based methods is a very active field.

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AF5-2 Toolbox for ALD Process Development on High Surface Area Powders

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Atomic layer deposition (ALD) is an industrially applied technique for thin film deposition with its origin in microelectronics.[1] Over the course of the past 50 years a wide variety of elements and combinations thereof were deposited *via* ALD.[2] However, the vast majority of processes targets flat substrates rather than powders. For ALD on powders, different reaction conditions are required and need to be identified for ALD to be applicable to high surface area powders. This work shows two setups in detail, which enhance the ALD process development for powders.[3] The first setup is capable of directly measuring the vapor pressure of a given precursor to pre-select promising precursors and their ideal saturation temperature. Afterwards, the second setup, consisting of four parallel reactors with individual temperature zones, is used to screen the optimal ALD temperature window in a time efficient way. Identifying the precursor saturation temperature beforehand and subsequently performing the first ALD half cycle in the parallel setup at four different reactor temperatures simultaneously will drastically reduce process development times. Validation of both setups is shown for the well-known ALD precursors trimethylaluminum to deposit aluminum oxide and diethyl zinc to deposit zinc oxide, both on amorphous silica powder. It can be shown that ALD on high surface area powders requires lower reactor temperatures than ALD on flat substrates. Furthermore, vapor pressures measurements of metal acetylacetonates revealed the need for elevated precursor temperatures for sufficient vapor pressures. There, to achieve reasonable vapor pressures of >10 mbar saturation temperatures of 100 °C are often needed.

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AF5-3 Tunable ALD Infiltration into Ultra-High-Aspect-Ratio Aerogels Enabled by Process Modeling for High-Temperature Solar Thermal Applications

Andrew J. Gayle, *Z. Berquist,* University of Michigan, Ann Arbor*; Y. Chen,* University of Michigan*; A. Hill, J. Hoffman, A. Bielinski, A. Lenert, N. Dasgupta,* University of Michigan, Ann Arbor

ALD provides a unique opportunity to impart conformal surface functionalization onto ultra-high-aspect-ratio structures, but depositions are complicated by precursor diffusion and dosing limitations. ALD modifications on substrates such as aerogels helps enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. In particular, SiO_2 aerogels possess a unique combination of desirable properties for CST applications, including high optical transparency and low thermal conductivity, but they suffer from poor stability at elevated temperatures. In this work, we investigate the ALD conditions needed to conformally coat SiO_2 aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. In order to minimize precursor waste during the long diffusion times necessary to conformally coat the AMs, we implemented a multi-dose-quasi-static-mode (multi-dose-QSM) deposition procedure. In standard QSM recipes, reactor pumping is halted during an "exposure step", allowing precursor to diffuse into a structure without being purged. In the multi-dose-QSM technique, multiple doses and exposure steps of a single precursor are implemented prior to dosing the counter reactant. This was necessary due to the large surface area of the AMs.

To enable tunable ALD infiltration depths into the AMs, we developed a model of the multi-dose-QSM deposition process. Building on previous work by Gordon [2] and Yanguas-Gil [3], our model accounts for precursor depletion in the ALD chamber during an exposure step and the effect of multiple precursor doses. This model also allowed for the optimization of the ALD coating process, including precursor usage efficiency and total process time.

SEM-EDS was used to quantify the ALD infiltration depth to validate the model. ALD saturation was further confirmed using mass gain measurements. After deposition, the AMs showed enhanced infrared light absorption while maintaining high visible light transparency after only one cycle of ALD Al_2O_3. The ALD-coated AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO_2 nanoparticle surface. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO_2 backbone and deposited Al_2O_3 film, as shown using XPS measurements. This combination of properties makes the ALD-coated AMs a promising transparent insulating material (TIM) for CST applications.

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AF5-4 Enhanced Throughput of High-Aspect-Ratio Atomic Layer Deposition Using Trimethylaluminum and Hydrogen Peroxide

Hideharu Shimizu, *T. Mizuno,* Taiyo Nippon Sanso, Japan*; D. Alvarez, J. Spiegelman,* RASIRC

Aluminum oxide (Al_2O_3) ALD has been studied and used for the mass production of devices. However, its long process time for high-aspect-ratio (HAR) structures is a critical drawback [1]. In this study, the reaction mechanism of Al_2O_3 ALD using trimethylaluminum (TMA) and H_2O_2/H_2O mixture [2] or H_2O was investigated; our results indicate that H_2O_2 could be purged more quickly than other reactants. Here, we used RASIRC's Peroxidizer™ to deliver the H_2O_2/H_2O mixture at a reproducible concentration. We demonstrated that the H_2O_2/H_2O mixture can shorten the purge period after a reactant feeding, leading to higher-throughput Al_2O_3 ALD for a HAR structure.

First, quantum chemical calculations and an exhaust gas analysis based on quadruple mass spectrometry were employed to study the reaction mechanism of ALD using the H_2O_2/H_2O mixture. A surface reaction between H_2O_2 and adsorbed TMA is expected to generate CH_3OH, which is thermodynamically favorable since the calculated reaction energy (ΔH) is -256 kJ/mol (Fig. 1). In addition, a surface reaction between H_2O and adsorbed TMA is expected to generate CH_4, for which the calculated ΔH is estimated to be -40 kJ/mol. In fact, using H_2O_2/H_2O, the exhaust gas analysis identified CH_3OH during reactant feeding step in ALD (Fig. 2a). CH_4, but not methanol, was observed in ALD using H_2O (Fig. 2b). These results indicate that the surface reaction in ALD using H_2O_2/H_2O is irreversible, while that using H_2O can be reversed to regenerate H_2O during the subsequent purge period.

Next, Al_2O_3 ALD was performed on a HAR structure (A/R ~100) using H_2O_2/H_2O mixture, H_2O, or O_3 with different purge periods and a reactant feed period of 10 s (Fig. 3a). Under these conditions, the conformality of the ALD was controlled by TMA diffusion. Conformality is generally worsened with a shorter purge period due to the formation of a reactive intermediate during precursor feeding [3]. In fact, when H_2O or O_3 was used as a reactant, ALD with the shorter purge period provided films with poorer conformality (Fig. 3b, c). However, using the H_2O_2/H_2O mixture with ALD reduced the purge period from 10 to 5 s without reducing conformality (Fig. 3d). This likely occurred because the irreversible reaction noted above prevented regeneration of H_2O_2/H_2O during the purge period. Thus, H_2O_2/H_2O is a promising reactant to enhance the throughput of ALD processes.

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ALD Fundamentals
Room On Demand - Session AF6
Growth and Characterization: Plasma Enhanced ALD

AF6-1 Plasma-Enhanced Atomic Layer Deposition: Correlating O_2 Plasma Parameters and Species to Blister Formation and Conformal Film Growth*, Andreas Werbrouck*, *K. Van De Kerckhove, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Plasma-enhanced ALD is now an essential part of the nanomanufacturing toolbox. Lots of processes have been reported and are used in production. Nevertheless, what happens in the plasma often remains a black box. Hence, it would be useful to have a basic insight in how plasma parameters affect the properties of the plasma and the resulting depositions. This way, partial pressure of active species can be increased, while possible damage to the films could be limited.

In this work, the effect of plasma parameters (power, pressure and flow) on the creation of plasma species was studied in a remote, inductively coupled oxygen plasma. In the plasma source region the O and O_2^+ production was characterized with optical emission spectroscopy (OES). In the remote region, near the substrate position we used an electrostatic quadrupole analyser (EQP) to measure energies and relative concentrations of O_2^+, O^+, O_2^- and O^-. Finally, a series of depositions with different plasma parameters was used to link these observations to growth and damage in actual ALD films.

An analysis of OES spectra (300-1000 nm) showed that a higher power linearly correlates with the concentration of created species. The O/O_2^+ ratio is determined by the flow and the power, and not so much by the pressure. The higher the flow, the higher the O/O_2^+ ratio. This is of relevance if we want to maximize the amount of radicals (for growth) or ions (for physically altering the film).

The EQP measurements at the substrate position show that the pressure is the determining factor for ions to reach the surface. The lower the pressure, the more ions can reach the surface. This may result in additional damage to the films. The influence of pressure on ions was dramatically illustrated with a series of depositions at different pressures with the gas coming from the side.

Finally, we deposited Al_2O_3 in lateral high aspect ratio structures with TMA and oxygen plasma at different powers and pulse times. The higher the partial pressure of reactive species near the entrance of the feature, the quicker the feature will be coated. We used a Markov chain simulation approach to quantify this. Simulated and fitted deposition profiles allowed us to estimate the partial pressure of active species in the plasma as a function of power and pressure. This analysis confirmed that higher plasma powers result in a higher partial pressure of reactive species.

With this research, we show that plasma parameters used in an PEALD process may strongly influence the growth and physical quality of the resulting film, especially on more challenging substrates.

AF6-2 Plasma-Enhanced ALD of TiN: Effect of the N-Source on the Growth and Quality of the Thin Films*, Clémence Badie,* CINaM , France*; T. Defforge,* GREMAN, France*; G. Gautier,* GREMAN , France*; L. Santinacci,* CINaM, France

The thermal ALD of TiN is well documented in literature. Various parameters of the process such as temperature or precursor pulse and purge durations have been deeply studied. The common precursor combination is TDMAT/NH_3, for thermal and for plasma-enhanced ALD. The PE-ALD recipe found in the literature [1] exhibits a longer cycle duration associated to a slower GPC regarding to thermal ALD. This can be detrimental for industrial production. In addition to NH_3, PE-ALD offers the possibility to use other N-sources: N_2, H_2 and N_2/H_2. The aim of this work is therefore to compare PE-ALD of TiN using two different N-sources to assess their effect on the final properties of the films and to shorten the deposition duration. The processes using NH_3 and N_2 combined with Ar are thus investigated in details and their growth rate is optimized. The influence of a set of parameters on the deposition process has been monitored by in situ characterizations (ellipsometry, OES) and the morphology, the composition, the crystalline structure and the electric properties of the films have been studied by ex situ techniques (TEM/SEM/AFM, XPS, DRX, 4-probes measurements).

To optimize the initial plasma-based recipe, the pulse and purge durations are investigated as well as additional parameters such as dilution of the N-sources within Ar and the plasma power. Those parameters are adjusted to limit the recombinations of the reactive species generated between the remote plasma source to the substrate. A large Ar dilution of both N_2 and NH_3 limits the film growth, a gas ratio of 1:1 for N-source and Ar flow is set to the optimal values. The pulse duration is shortened, 2 and 5 s for NH_3- and N_2-based plasmas, respectively. Saturation is assessed adjusting the purge duration optimum. The applied power (50 to 300 W) has no significant effect on the GPC with NH_3 plasma while, for N_2-based plasma, the GPC is maximum at the highest power. This is consistent with the expected low reactivity of N_2 (inert without plasma activation) as compared to highly reactive NH_3. Those results indicate that producing less active species facilitate their transport by limiting the recombinations. The films grown from both N-sources have a similar roughness, composition and morphology. However, the conductivity, conformality on high aspect ratio substrates and the growth rate are better using NH_3-based plasma. The N_2 plasma process exhibits an acceptable film quality and it should be considered as since it uses a non-harmful gas.

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AF6-3 Plasma Treatment to Tailor Growth and Photoelectric Performance of Plasma Enhanced Atomic Layer Deposition SnOx Transparent Conductive Thin Films*, Liangge Xu,* Harbin Institute of Technology, China

Transparent conducting oxides (TCOs) are widely used materials with high optical transparency and electrical conductivity. SnO_2 is an n-type semiconductor material with high carrier concentration and low resistivity. Currently, further development and application of tin-doped indium oxide is limited by the high cost and rarity of indium. Alternatively, Tin dioxide (SnO_2), which is a low-cost, non-toxic, and abundant material, has been extensively studied for its optical and electrical properties, which are comparable to those of indium oxide. More recently, SnO2-based materials, such as ATO (Sb-doped SnO_2) and FTO (F-doped SnO_2), have attracted considerable attention in theoretical and experimental studies. Improved crystallinity by mild plasma bombardment of surface molecular structure is practical. Crystallization by plasma treatment is advantageous in that it can be implemented in-situ, does not need an elevated temperature, and reduces preparation time.Low ion density and nondestructive crystallization of films make remote plasma ALD a promising process for future use.

The performance of atomic layer deposition films is mainly limited by precursor residues, low crystallinity, and densities due to low deposition temperatures. Here, we used atomic layer deposition to deposit tin oxide thin films at a relatively low temperature of 250 °C. At this temperature, the change in the valence of Sn due to precursor residue is eliminated by layer-by-layer Ar plasma treatment, and the crystallinity of the films is improved. The effects of Ar plasma treatment power and Ar treatment time on the structural and optoelectronic properties were investigated. It was found that Ar plasma treatment time more significantly affects the surface morphology and the optical and electrical properties of the film. The film is transparent to both visible and near infrared light over a wide range of wavelengths from 400 nm to at least 5000 nm. The film resistivity can be as low as $1.117\times10^{-3}\Omega\cdot$cm. The film has a relatively low level of residual stress due to the fact that there is no need to improve the crystallinity of the film by conventional high temperature annealing. On the basis of the high transparency and high conductivity of the SnOx films with layer by layer Ar plasma treatment in situ, the films can be applied as electromagnetic shielding windows for photodetectors.

AF6-4 Plasma-Induced Local Crystallization of ALD TiO_2 Films*, DOHYUN GO*, *J. SHIN, . LEE, J. AN,* Seoul National University of Science and Technology, Korea (Republic of)

Titanium oxide (TiO_2) films get much attention in various fields because of their unique properties including high permittivity, chemical stability, non-toxicity, and low cost. Interestingly, crystallinity and phases affect the properties of TiO_2 films. For instance, the dielectric constant of amorphous TiO_2 is lower than 30, but anatase and rutile show a much higher dielectric constant (anatase: 30-75 and rutile: 90-170). Simultaneously, the grain boundary formation of crystalline TiO_2 can also be an electron conduction path leading to high leakage. Atomic layer deposition (ALD) is known to form the thin-film at much lower temperature regime (<300℃) than chemical vapor deposition (CVD). Lowering the deposition temperature can increase the types of available substrates such as polymer and organic substrates, but may hamper the crystallization of thin-films. In this regard, additional processes are necessary for crystallizing thin-film and modifying the electrical/optical properties. Annealing (e.g., rapid thermal annealing (RTA)) and seed-layering (e.g., deposition on the crystalline seed) are representative methods. However, high process temperature (>500℃) and material selection are limits of those methods.

Recently, thin-film crystallization using plasma treatment has been actively researched in plasma-enhanced ALD (PEALD). Plasma-induced crystallization proceeds by ion bombardment of highly reactive ions and radicals inside the plasma and transferring kinetic energy through the thin-film surface. Plasma-induced crystallization can minimize thermal damage and be free of material selection. However, the relatively high oxidation power of plasma compared to the oxidant typically used in thermal ALD (e.g., H_2O, O_2) can develop the unwanted interfacial layer, which decreases the device performance, especially when the interface property between film and substrate is important.

In this study, we precisely modulate the film properties (physical, optical, and electrical) by controlling the crystallinity of TiO_2 thin-film along the thickness direction. We stack the amorphous TiO_2 and crystalline TiO_2 with varying ratios (so-called vertical phase-gradient film). The thickness ratios of amorphous TiO_2 and crystalline TiO_2 are accurately adjusted using extremely-localized plasma-induced crystallization by *per-cycle* plasma exposure. The physical and optical properties are precisely modulated depending on the ratio. Furthermore, we figure out the optimal ratio of amorphous TiO_2 and crystalline TiO_2 for the high dielectric constant and low leakage current.

AF6-7 In-situ Photoemission Study on the Growth of Cobalt Nitride through PE-ALD*, Matthew Snelgrove*, *K. Shiel, E. McGlynn, R. O'Connor,* Dublin City University, Ireland

This work provides new insights into the nucleation and growth characteristics of thin cobalt nitride films deposited by plasma enhanced ALD. The material has applications in CMOS processing for promoting Cu interconnect adhesion and in renewable energy fields as a metallic electrocatalyst.[1,2]Cobalt Nitride, while successfully grown via PE-ALD using several Co-based precursors and co-reactant gases, has presented interesting results where the deposited film can contain large amounts of carbon impurities.[3] Additionally, the effect of deposition temperature has been reported to have a drastic impact on the stoichiometry of the resulting films.[4]

By using an integrated XPS/ALD system, which allows for rapid photoemission analysis during an ALD process without the need to leave high vacuum, the growth characteristics of CoN using the precursor Cobaltocene ($CoCP_2$) with ammonia plasma as co-reactant is studied without complication of the results by atmospheric carbon and oxygen contamination. We examine the impact of the temperature and plasma pulse duration on the film composition and show that rather than displaying saturation, longer plasma pulses severely inhibit the growth rate at all temperatures. The optimum plasma pulse duration for maximum growth per cycle is shown to reduce with increasing temperature. The *in-situ* approach combined with high-energy synchrotron-based photoemission studies of the resulting films enables understanding of the bulk properties without need for physical removal of matter by sputtering. Our results provide an insight into optimising PE-ALD processes for deposition of cobalt nitrides and strategies for minimizing carbon incorporation from the $CoCP_2$ precursor ligands.

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AF6-10 Atomic Layer Doping of β-Ga_2O_3 Films via Plasma Processing*, Saidjafarzoda Ilhom*, *A. Mohammad, D. Shukla, J. Grasso, B. Willis, A. Okyay, N. Biyikli,* University of Connecticut

Gallium oxide (Ga_2O_3) is an emerging ultrawide-bandgap (UWBG) semiconductor attracting significant interest for high-power and high-frequency electronics that features comparable electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm) to wide-bandgap GaN and SiC. However, growing device level high-quality (Ga_2O_3) films have been mainly possible using high-temperature requiring harsh environments (700 – 1000 °C), which substantially limit its application space. In this work, we report on the low-temperature deposition of β-Ga_2O_3 films on Si, sapphire, Kapton, and glass substrates coupled with *in situ* atomic layer doping using hollow-cathode plasma-enhanced ALD. The films were deposited using triethylgallium (TEG) and Ar/O_2plasma as metal precursor and oxygen co-reactant, respectively, whereas tris-dimethylaminosilane (3DMAS) was utilized as the n-type dopant precursor. Growth experiments have been performed at 200 – 240 °C substrate temperatures and 50 W rf-power level. The doping process was carried out via both co-dosing (where the dopant is pulsed together with the metal precursor) and super-cycle (ABC-type ALD-cycle) methods. Additionally, each unit ALD-cycle was followed by an *in-situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both *in-situ* and *ex-situ* ellipsometry were employed to measure the thickness and optical properties of the films. The samples grown without Ar-plasma annealing step exhibited amorphous character with a growth-per-cycle (GPC) of 0.69 Å/cycle. However, with the incorporation of the *in situ* Ar-plasma annealing process crystalline films showing monoclinic β-Ga_2O_3 phase were achieved showing a GPC of ~1.04 Å/cycle. X-ray photoelectron spectroscopy (XPS) measurement of the β-Ga_2O_3 sample grown under optimal *in situ* plasma annealing power (250 W) revealed near-ideal film stoichiometry (O/Ga of ~1.44) with relatively low carbon content (~5% at.). Our results demonstrate the effectiveness of *in situ* Ar-plasma annealing process to transform amorphous wide bandgap oxide semiconductors into crystalline films without needing high-temperature post-deposition annealing treatment. Further outcomes from our ongoing atomic layer doping experiments featuring co-dosing and super-cycle techniques followed by additional structural, optical, and electrical characterizations will be discussed as well, which provide additional insight to overcome the challenges in achieving device quality β-Ga_2O_3 layers on low-temperature compatible substrates.

AF6-13 Electron Enhanced Atomic Layer Deposition of Aluminum Phosphide with Trimethylaluminum and Tritertbutylphosphine*, SeongUk Yun*, *A. Kummel, S. Ueda, V. Wang, C. Kuo, H. Kashyap, A. Mcleod,* University of California, San Diego, USA

Aluminum phosphide (AlP) is an interesting wide bandgap III-V semiconductor with applications in optoelectronics, small lattice-mismatch regarding GaP/Si, and potential use as X-ray multi-layer mirror[1]. Most AlP films have been deposited using the chemical vapor deposition processes (CVD) with PH_3. High-quality AlP films require the high partial pressure of PH_3, which is highly toxic. Terada et al. investigated the 500°C CVD AlP with trimethylaluminum (TMA) and Tritertbutylphosphine (TBP), which is safer than PH_3[2]. Gudovskikh et al. reported that nanocrystalline GaP was grown at 380°C using plasma-enhanced atomic layer deposition (PE-ALD) with trimethylgallium and PH_3 in an H_2 purge[3]. However, AlP deposition using ALD process has rarely been investigated yet since it is highly reactive toward moisture and difficult to crystallize.

The major challenge in TMA + TBP ALD process is the low reactivity of the TBP precursor. High process temperature (>500°C) and substrate atomic H bombardment have been shown to improve reactivity, but ALD of related compounds shows there may be alternatives. For example, Sprenger et al. reported that electron enhanced ALD (EE-ALD) improved the growth rate of GaN film at below 100 °C.

The low-temperature (≤ 400°C) ALD of AlP on III-V semiconductors was investigated using three techniques: thermal ALD, atomic layer annealing (ALA), and EE-ALD [4]. TMA and Tri(dimethylamido)aluminum(III) (TDMAA) were employed as Al precursor and TBP was employed as the phosphorus precursor. The films were characterized with in-situ Auger and ex-situ atomic force microscopy (AFM).

Table 1 summarized the atomic composition in the AlP films from in-situ Auger analysis of the AlP ALD and AlP ALA at 300°C with TDMAA and TMA, respectively. Si composition in AlP in ALA was lower compared to that in AlP ALD, suggesting improved AlP growth rate with ALA process. Figure 1 (a) showed that P/Al atomic ratio increased up to 0.8 in AlP EE-ALD process. This suggested AlP films with high P/Al=0.8 were prepared using EE-ALD with TBP precursor at 300°C. The atomic compositions of AlP EE-ALD process at different temperatures are shown in Figure 1 (b). Large size (≥ 15 nm) of islands of AlP film in Figure 2 (a) and low P/Al=0.5 indicated the formation of AlPOx nanoparticle of AlP ALD due to the insufficient nucleation of TBP at 210°C. AlP films at 300°C and 400°C showed high P/Al = 0.8. While Figure 2(b) showed the amorphous AlP film at 300°C, the high-quality (~P/Al=0.8) and nano-crystallized (RMS=0.9 nm) AlP films were successfully deposited by EE-ALA at low temperature (≤ 400°C) using TBP precursor.

AF6-16 Tuning the Structural Properties of Low-Temperature Grown GaN Films via *in Situ* Ar-Plasma Annealing During Hollow-Cathode Atomic Layer Deposition*, **DEEPA SHUKLA**, N. Biyikli,* University of Connecticut

Future energy efficient devices and will feature wide bandgap semiconductors allowing greater power efficiency, smaller size, lighter weight, lower overall cost. GaN among the other wide bandgap materials, has a large bandgap (3.4 eV) and when compared to the conventional electronics material of choice Si, the critical breakdown field is an order of magnitude higher and the achievable electron mobility (2DEG mobility in AlGaN/GaN HEMT structures) is nearly double. Both the output charge and gate charge are ten times lower than with Si, and the reverse recovery charge is almost zero which is key for high frequency operations. Owing to these attractive properties and features, GaN is used in a variety of microwave power applications due to their superior electron transport properties.

In this work, we report on the low-temperature, as-grown crystalline GaN films on various substrates via a hollow-cathode plasma-ALD system. The purpose of this work is to see the effect of different plasma gas mixture on the growth of GaN films at substrate temperatures less than 250oC and tune the crystallinity via in situ Ar-plasma annealing.

Plasma assisted atomic layer deposition of GaN thin films is carried out in a hollow cathode plasma-ALD chamber. Si (100), Si (111), glass, and sapphire films have been used as the substrate. The growth temperature is kept between 120 to 240 °C, 10 sccm of N2 flow is used as a carrier gas and Ar-purging gas flow at 50 sccm. Triethylgallium is used as Ga precursor and various nitrogen plasma chemistries including different compositions of N2, H2, and Ar gases are studied. The optimized growth condition is determined from the saturation studies, where the growth-per-cycle (GPC) parameter is noted for different precursor pulse time (30, 45, 60 and 90 ms), rf-plasma power (100 W to 200 W) and plasma-gas chemistries at different plasma compositions have been studied at (i) Ar/N2 at 50/50 sccm; (ii) N2-only at 50 sccm; and (iii) N2/H2 at 50/10 sccm. We observed the crystalline nature of GaN films through XRD analysis. The as-grown films were compared with films grown with an additional Ar-plasma annealing step within the unit-ALD cycle. As we recently reported for Ga2O3 films, our main goal is to achieve improvement in crystalline properties with the surface heating effect of the in situ Ar-plasma annealing treatment. The XRD measurements of these in situ Ar-plasma annealed samples will be presented along with the spectroscopic ellipsometer, x-ray reflectivity (XRR), and x-ray photoelectron spectroscopy (XPS) studies. The impact of the reactor ambient during plasma annealing under different plasma gas mixtures will be presented as well.

AF6-19 Optimization of AlN Film Purity Using Atomic Layer Annealing*,* ***Markus Bosund****, E. Salmi, K. Väyrynen, M. Söderlund,* Beneq, Finland*; P. Rabinzohn,* Beneq, France*; M. Heikkilä,* (2) University of Helsinki, Department of Chemistry, Finland*; J. Julin,* (3) University of Jyväskylä, Department of Physics, Finland*; T. Sajavaara,* University of Jyväskylä, Department of Physics, Finland

Aluminum nitride (AlN) combines a high band-gap with good thermal conductivity making it an excellent material for several applications. AlN films are being considered as passivation and dielectric layers for power devices and other compound semiconductor devices such as RF, VCSEL, LED, and Light Sensor. Both bulk film and boundary impurities affect the device performance. This study presents observations of Atomic Layer Annealing (ALA) on PEALD AlN film and interface impurities. Less examined hydrogen impurity level was also measured from the films.

Atomic layer annealing is a method where additional thermal energy is introduced after each ALD cycle. In this work the ALA step was done using an additional plasma pulse. Earlier studies indicate that epitaxial growth can be reached with plasma ALA step **[1-3].** Although this method has been demonstrated earlier, the effect of ALA step on atomic concentrations and especially film hydrogen concentrations and especially film hydrogen concentration are published for the first time.

This research work also presents a slightly different simplified process using only N_2 gas in the ALA step instead of Ar or Ar/N_2 mixture. The difference of AlN films deposited with and without ALA steps were investigated using X-ray diffraction (XRD) and Time-of-flight elastic recoil detection analysis (TOF-ERDA) spectrometer for elemental analysis.

AlN purity variation within wafer was also investigated. Atomic concentrations were measured from 200 mm wafers. Three measurement points were taken at precursor flow direction.

Beneq TFS 200 and Transform^{TM} reactors equipped with direct CCP plasma were used in this work. Plasma frequency was 13.56 MHz. Ammonia plasma was used in ALD step but ALA step was done using N_2 as presented in Fig. 1. (supplemental file). Various plasma times and reactor temperatures were investigated.

ALA step had clear effect on the crystalline structure of the AlN film. All films were polycrystalline hexagonal wurtzite aluminum nitride layers but the films deposited with ALA step had stronger (002) preferential orientation.[1,3]

TOF-ERDA elemental analysis indicated that the atomic concentration of hydrogen decreased from 12 to 7 at.-% with ALA step. This difference was obtained from the bulk of the film. Oxygen impurity was optimized below 0.5 at.-% and carbon impurity always lower than 1.2 at.-%

AF6-22 Understanding the Influence of Plasma-Enhanced Atomic Layer Deposition of SiN on GeSbTe*,* ***Hamid Razavi****,* University of California, Los Angeles*; M. Shen, J. Hoang, T. Lill,* Lam Research Corporation*; J. Chang,* University of California, Los Angeles

Keeping the composition of $Ge_xSb_yTe_z$ (GST) materials constant during the encapsulation process is a challenging problem mostly due to the volatility of Ge products during the deposition processes particularly at higher temperatures between 100 and 150^{o}C.

This work studies the effect of the Ge, a constituent element of GST, as a model substrate on the nucleation and growth behavior of SiN capping layer deposited by plasma-enhanced atomic layer deposition (PE-ALD) method using Bis(t-butylamino)silane (BTBAS) with the molecular formula of $[NH(C_4H_9)]_2SiH_2$ as the Si precursor. Atomic nitrogen generated by a 2.45 GHz coaxial waveguide microwave plasma source was used as a nitridizing agent of the precursor.

The deposition of PEALD SiN was assessed by examining the effect of substrate temperature (25 to 150^{o}C), microwave plasma power (25 to 75 W), and the pre-deposition plasma surface treatment. The in-situ N_2 plasma was effective for substrate cleaning by reducing O concentration from the Ge native oxide layer. The nucleation and the growth of deposited SiN on the substrates was studied using an in-situ x-ray photoelectron spectroscopy and ex-situ scanning electron microscopy (SEM). The relative concentration of nitrogen atoms was quantified as a function of plasma processing parameters by optical emission spectroscopy as it dictates the surface reaction with the precursor to form SiN. XPS results confirmed the nucleation of Si_xN_y with the ratio of x/y=1/2 on Ge/GeO_2. Pre-deposition N_2 plasma surface treatment resulted in nitridation of Ge and a significant reduction of the oxygen and carbon content, making the interface a higher quality one

AF6-25 Low-Temperature Plasma Enhanced Atomic Layer Deposition of WO_x using a novel Tungsten Precursor, *Kamesh Mullapudi*, *K. Holden, J. Peterson,* Oregon State University*; R. Kanjolia, D. Moser, C. Dezelah,* EMD Performance Materials*; J. Conley,* Oregon State University

Tungsten oxide (WO_3) has garnered interest lately for its use in smart windows,[1] forming-less resistive memories,[2] and as a potential candidate for emerging neuromorphic memories.[3] Microelectronics applications require films of high electrical quality with excellent conformality, uniformity, and thickness control for which ALD is the method of choice. Early thermal ALD reports of WO_3 films employed the use of halide-based precursors which resulted in self-etching due to reaction byproducts.[4,5] More recent work has focused on metal-organic chemistries and plasma-enhanced ALD (PEALD), which provides benefits such as lower deposition temperatures. Recent PEALD work includes $WH_2(iPrCp)_2$ and $W(tBuN)_2(Me_2N)_2$ with a direct O_2 plasma source which required temperatures in the range of 300-400°C for a constant GPC window.[6,7] Another recent study used $WH_2(Cp)_2$ with a remote O_2 plasma and reported a constant GPC ALD window between 200-300°C and that O-content could be controlled with H_2 plasma in an ABC type process.[8]

In this work we report PEALD of WO_3 using a novel metal-organic tungsten precursor [bis(tert-butylimido)bis(trimethylsilylmethyl)tungsten(VI), $W(CH_2Si(CH_3)_3)_2(CN(CH_3)_3)_2$ or WSN-4] with remote O_2 plasma as a co-reactant using a Picosun R200 reactor. A plot of film growth per cycle (GPC), using a 2/15/40/30 s WSN-4/N_2/O_2 plasma/$N\text{-}_2$ pulse sequence, shows growth decreasing from 1.0 to 0.44 Å/cycle as the growth temperature increases from 150 to 350°C, accompanied by an increase in optical refractive index from (Fig. 1). Pulse saturating behavior for both the WSN-4 (Fig. 2) and O_2 plasma (Fig. 3) half-cycles, indicates that film growth is self-limited at 250°C. Grazing angle x-ray diffraction (GI-XRD) reveals that an as-deposited 12 nm thick film was amorphous, while post-deposition isochronal (60 min) O_2 annealing produced crystallization at 600°C into the triclinic phase of WO_3, with an estimated grain size of ~30 nm (Fig. 4 and SEM image inset).

Further details on WSN-4 properties, nucleation behavior on BEOL metals such as TiN and TaN, film density, stoichiometry, band gap, and electrical properties of ALD WO_3 will be discussed at the meeting.

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ALD Fundamentals
Room On Demand - Session AF7
Growth and Characterization: Low Temperature ALD

AF7-1 Neutral Beam Enhanced Atomic Layer Deposition at Room Temperature for Si Dielectric Film, *Ge Beibei,* Tohoku University, Japan, China*; C. Hua Hsuan,* National Yang Ming Chiao Tung University , Taiwan*; O. Daisuke, O. Takuya, S. Seiji,* Tohoku University, Japan

Atomic layer deposition (ALD) is a synthesis thin film technique based on sequential, self-limiting reactions which has developed significantly in recent years [1]. Silicon dielectric films such as silicon dioxide (SiO_2) films and silicon nitride (SiN) films can be deposited using several ALD techniques, such as thermal ALD and plasma-enhanced ALD. The high deposition temperature and high thermal budgets have become a problem of traditional thermal ALD, the deposited films show low quality and poor step coverage [2]. PEALD could deposit at lower temperature, but inherent problems in plasma process such as plasma irradiation and charge accumulation will cause defects on films [3]. In previous report by Samukawa et al, using O_2 neutral beam could synthesize the very high quality SiO_2 film on the Si substrate at room temperature [4]. In this work, we demonstrated growth of Si dielectric thin films by neutral beam enhanced atomic layer deposition (NBEALD) at room temperature.

Thin SiO_2 and SiN films were deposited on Si substrate at 30°C using bis(diethylamino)silane (BDEAS) as Si precursor, O_2 or N_2 as the neutral beam gases. The NBEALD cycle was composed as follows: precursor absorption, purge, reactive gases injection, neutral beam irradiation and purge. In this process, neutral beam instead of plasma was used in irradiation step of ALD for providing energy on surface reactions. The thickness of NBEALD Si dielectric films was measured by spectrum ellipsometer. Film quality was investigated by X-ray photoelectron spectroscopy (XPS) to analyze the element composition. The density of the Si dielectric films was studied by x-ray reflectivity (XRR). The surface roughness of the deposited films was investigated by atomic-force microscope (AFM).

SiO_2 films with high quality in terms of chemical composition, surface roughness and mass density are equivalent to that of thermal oxidation films. For the growth of SiN film, the growth per cycle of the feed time was saturated over the 2 sec. The deposition rate was 0.32 Å/cycle. For the XPS results, SiN film showed the strong $N\text{-}Si_3$ peak at 397.5 eV. On the other hand, weak $C\text{-}NH_2$ peak at 399.7 eV, and C=O peak at 531.5 eV were observed. As a result, it suggests that the carbon contamination was amide group that comes from precursor. It can be solved to optimize the NB source power and bias power condition. Hence, N_2 neutral beam with BDEAS achieved the SiN film growth at room temperature.

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ALD Fundamentals
Room On Demand - Session AF8
Growth and Characterization: *In-situ* Monitoring and Analysis

AF8-1 Optimization of Quadrupole Mass Spectrometers for In-situ Monitoring of Atomic Layer Deposition Processing, *Chenglong Yang*, *J. Blessing,* MKS Instruments, Inc.*; U. Meissner,* MKS Instruments, Inc., Germany*; A. Wallace ,* MKS Instruments, Inc., UK

Quadrupole Mass Spectrometers (QMS) have been used widely in atomic layer deposition (ALD) for process optimization and troubleshooting. Unfortunately, QMS has had little application for in-situ process monitoring owing to its short lifetime and less persuasive value of process monitoring. This study is to improve the QMS sampling system design for ALD processes, which includes the ALD gas sampling and delivery, inlet valve design, and the range and control of the sampling system temperature. In addition, the QMS hardware and operating methods are also upgraded to improve the sensitivity and its lifetime for ALD processes. This QMS system has been applied to ALD processes for in-situ monitoring of chamber base vacuum, ALD precursors, process reaction by-products, and chamber contamination.

AF8-2 Quantitative Calorimetry of ALD: Design, Model, and Calibrate, *Ashley Bielinski*, *A. Martinson,* Argonne National Laboratory

Pyroelectric calorimetry presents a new approach for the *in situ* study of the thermodynamics and kinetics of ALD reactions with unmatched thermal sensitivity and temporal resolution. Complementary techniques such as quartz crystal microgravimetry, spectroscopic ellipsometry, and mass spectrometry are limited by sampling times that are typically on the order of 50ms – 1s. We demonstrate response times down to 50ns and sensitivities of < 1µJ/cm², which corresponds to less than 1% of the heat generated by some ALD half reactions.

Large temperature changes, >10°C, as a result of ALD surface reactions have been observed on high surface area substrates. However, attempts to quantitatively measure reaction heats on planar substrates, ≪1°C, using thermocouples or pyroelectric detectors have previously been limited by hardware with insufficient thermal and temporal resolution, difficulties accounting for heat lost to cooling, and challenges with external calibration. To overcome these issues we designed and built pyroelectric calorimeters compatible with ALD systems, modeled the transient thermal and electric response, and quantitatively calibrated the system using a laser to provide precise heat generation.

This work was inspired by the techniques used in pyroelectric adsorption calorimetry, but the approaches used in this field resulted in unacceptable tradeoffs in responsivity in order to achieve the temporal resolution needed for ALD. A new calorimeter design was implemented to suspend the pyroelectric crystal with minimal physical contact. This reduced conductive cooling, enabling improved temperature sensitivity and faster responsivity.

Previously, ALD reaction energies have been computationally predicted, but not experimentally measured. ALD calorimetry contributes a new experimental technique with a wide range of applications including the study of fundamental reaction thermodynamics, the impact of non-ideal surfaces on nucleation, selective defect passivation, and growth inhibition.

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AF8-3 Atomic Layer Deposition of Hafnium Oxide on InAs: Insight from Time-Resolved *in Situ* Studies

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Despite the numerous applications of atomic layer deposition (ALD), used e.g. in the semiconductors industry to produce thin films with thickness control at the Ångström level and tunable composition, only limited knowledge exists about the kinetics of the surface chemical reaction, the reaction mechanism, and the role of the substrate. ALD-grown thin high-k oxide films, such as HfO_2 or Al_2O_3, help to significantly improve device performance of III-V semiconductor-based MOSFETs. Those materials, such as InAs, come along with an electron mobility 20 times larger than that of silicon, but unfortunately with a high defect density at the interface with its oxide. It has been demonstrated that so-called "self-cleaning" occurs during the early stage of the high-k ALD, in which the growing high-κ oxide substitutes the unwanted native oxide. However, in spite of all progress, the III-V/oxide interface still suffers from incomplete self-cleaning and too high defect levels.

In this work, we present a time-resolved study of the self-cleaning effect during the first ALD half cycle. We performed ALD of HfO_2 on InAs in the reaction cell of a synchrotron-based ambient pressure X-ray photoemission spectroscopy (APXPS) setup. Tetrakis(dimethylamido)-hafnium (TDMA-Hf) is used as the metallorganic precursor, and we followed in real time all relevant core levels to monitor the surface species during the deposition. Our findings challenge the established view of the ALD process based on the ligand exchange model and the surface's passive role. In fact, we establish a two-step reaction based on molecular adsorption followed by ligand exchange and the immediate formation of HfO_x, in which the native oxide acts as the oxygen source. In more detail, we find evidence for an As-In-O-Hf bonding configuration at the semiconductor/high-k interface.

Hence, time-resolved APXPS enables us to further understand the surface chemical process in ALD and how the III-V semiconductor/high-k interface can further be improved by optimizing ALD, promising superior device performance.

ALD Fundamentals
Room On Demand - Session AF9
Growth and Characterization: Characterization of ALD Films

AF9-1 Smoothing Surface Roughness Using Al_2O_3 Atomic Layer Deposition

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Surface roughness can affect many areas such as optical scattering, friction, adhesion and semiconductor device performance. There are various methods for smoothing surfaces including chemical mechanical polishing (CMP) and chemical etching. However, these methods are abrasive and corrosive and can be detrimental. Atomic layer deposition (ALD) deposits conformal films that can “pinch off” surface roughness by filling in the gaps between surface asperities. In this study, Al_2O_3 ALD was used to smooth rough silicon wafers and improve the optical reflectivity of Ag mirrors deposited on the silicon wafers.

Al_2O_3 ALD was performed on rough, pre-CMP silicon wafers. Al_2O_3 was deposited at 200°C using trimethylaluminum (TMA) and water (H_2O) as the reactants. Al_2O_3 ALD films of various thicknesses were grown on the silicon wafers using up to 4000 Al_2O_3 ALD cycles. The RMS roughness was measured using atomic force microscopy (AFM). AFM showed that the original rough, pre-CMP silicon wafers had an RMS roughness of 3.5 nm. AFM line scans measured an average lateral spacing between the surface asperities of 400 nm (Figure 1a). After 3000 Al_2O_3 ALD cycles, the RMS roughness of the wafers was reduced to 1.5 nm and the average lateral spacing between the surface asperities increased to 700 nm (Figure 1b).

The RMS roughness decreased progressively with number of Al_2O_3 ALD cycles (Figure 2). The minimum surface roughness of 1.5 nm was reached after 3000 cycles. Additional Al_2O_3 ALD cycles then produced little change in the RMS roughness. The smoothing is believed to limit when the lateral distance between the surface asperities is much larger than the Al_2O_3 ALD film thickness. Power spectral density (PSD) analysis revealed that the ALD smoothing was most effective for surface topographical features with lateral spacings in the range of 10s to 100s of nanometers. The PSD analysis showed that most of the smoothing occurs during the first 1000 Al_2O_3 ALD cycles. Reflectivity studies of Ag mirrors deposited on the silicon wafers demonstrated that Al_2O_3 ALD smoothing improves the optical performance of reflective mirrors.

AF9-2 Effect of Oxidant on Film Properties of HfO_2 grown via Atomic Layer Deposition using Newly Synthesized Cp-based Hf Precursors

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With the scaling down of semiconductor devices, SiO_2 was replaced by high-k materials due to increased leakage current. Among the various high-k materials, HfO_2 has been widely used owing to its high dielectric constant (~25) and suitable band offset with Si (~1.4 eV).[1] For ultrathin high quality HfO_2, atomic layer deposition (ALD) has been used. Through ALD technology, atomic layer controlled HfO_2 film with high conformality and high uniformity can be obtained. For HfO_2 ALD technology, various precursors such as halides, alkoxides, alkylamides, and β-diketonates have been applied. Using halide precursor, HfO_2 films do not have C impurities. However, corrosive byproducts such as HCl can degrade the film quality.[2] Furthermore, halide precursors have low volatility which means that high temperature is needed to get HfO_2 films.[2] Alkoxides have strong metal-O bonds, so that they require high temperature for deposition process. In addition, β-diketonates are not proper precursors for ALD, because they have bulky ligands which leads to steric hindrance and have low volatility.[1] β-hydride elimination causes hydrolytic decomposition of β-diketonates, which leads to the non-saturated growth characteristics. Since alkylamides have weak metal-N bonds, they are highly reactive at low temperature. Although alkylamides are widely used for ALD process, they are easily decomposed at high temperature.[1] Therefore, there can be a lot of impurities on thin films deposited with ALD. By employing cyclopentadienyl (Cp) ligand as functional ligand group of heteroleptic precursor, thermal stability and volatility of alkylamide precursors are improved.[1] Research has been conducted to increase thermal stability of precursors by increasing the number of Cp ligands. However, even that has now reached its thermal stability limit, requiring a precursor available at higher temperatures. We newly synthesized the Hf precursor which is stable at higher temperature. We investigated the effect of oxidants on film properties of HfO_2 using newly synthesized Cp-based alkylamide Hf precursor.

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AF9-3 Advanced Wafer Scale Uniformity Characterization Method for Conformal 3D Thin Films

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Atomic layer deposition (ALD) enables uniform thin film coating over large substrate areas. Besides thickness uniformity, today’s memory and MEMS applications with three-dimensional structures require good conformality over high aspect ratio (HAR) structures. The state-of-art method to define wafer scale uniformity is film thickness mapping. Easy wafer level conformality characterization from 3D HAR structured wafers is hardly accessible due to challenging high-resolution cross-sectional measurements. PillarHall® Lateral High Aspect Ratio (LHAR) silicon test chip has already proven its value in conformality metrology and even in the characterization of the thin film properties inside deep cavity walls [1,2,3] without cross-sectioning. The purpose here is to study further the consistency, sensitivity and accuracy of the wafer level uniformity and conformality analysis using PillarHall® LHAR4 test chip (Chipmetrics Ltd) on 150 and 200 mm silicon carrier wafers. Chips were placed evenly over the studied substrate area. An analysis was made using simple optical measurement tools such as optical modelling software, optical microscopy with image analysis, and reference reflectometry measurements. Experimental work consisted of several thermal ALD processes (Al_2O_3, SiO_2, TiO_2 and TiN). ALD reactors were Picosun R-150 and Beneq TFS-200. Optical microscope image analysis was used to assess conformality analysis accuracy using ALD Al_2O_3 on LHAR samples from various positions of the wafer area. The results show good accuracy and are in line with optical modelling outcome and in agreement with reflectometry data. Optical modelling also enables predictions of the method compatibility and limitations with various other thin-film materials. When comparing the ALD Al_2O_3 data to the simultaneous flat substrate thickness mapping, it is shown that PillarHall® method is a sensitive measure for wafer-level uniformity and conformality mapping. The presented method is widely compatible to ALD and related 3D thin film processes and can accelerate their industrial applications.

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AF9-4 Thermal Atomic Layer Deposition of Silicon Nitride Using Anhydrous Hydrazine and Ammonia

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In this study, a thermal atomic layer deposition (t-ALD) for silicon nitride (SiN_x) is established at the temperature window of 320–600°C. Hexachlorodisilane (HCDS) and high purity anhydrous hydrazine (N_2H_4) are utilized as the precursors for silicon and nitrogen, respectively. The characteristics of deposited films are analyzed by the growth per cycle (GPC), refractive index (R.I.), wet-etch rate (WER), and chemical composition. The electrical properties of SiN_x deposited using N_2H_4 are also studied using "metal-insulator-metal (MIS)" structure. *-in-situ* FTIR technique is employed to examine the bonding information.

At 480°C, the GPC of silicon nitride gradually increases with an increase in the N_2H_4 pulse time (0.2, 0.5, 1.0, and 2.5 s). SiN_x exhibits a growth rate of 0.031 nm/cycle with 0.5-second N_2H_4 exposure time at the working pressure of 150 mTorr. At the same deposition temperature (480°C) and hydrazine exposure time (0.5 s), the GPC at 500 mTorr is 0.048 nm/cycle. Within the temperature range of 390–520°C, the growth per cycle is nearly constant, with the approximate value of 0.049 nm/cycle. Furthermore, silicon nitride thin films are also grown using ammonia (NH_3) as references. Under identical deposition conditions (exposure time, temperature, and working pressure), ammonia delivers a lower growth rate (~0.019 nm/cycle) than hydrazine. As the deposition temperature increases, the refractive index of SiN_x grown with hydrazine increases (as high as 1.99), while the WER significantly decreases with the etch rate as low as 0.37 nm/min in 200:1 HF diluted solution. At 480°C, silicon nitride grown using hydrazine and ammonia has a density of 2.73 and 2.69 g/cm^3, respectively. The R.I. and WER values are 1.86 and 2.24 nm/min for hydrazine, while 1.96 and 7.48 nm/min for NH_3. The chemical composition of SiN_x grown with N_2H_4 is 54±1.0 [Si] at.%, 44±1.0 [N] at.%, 2±1.0 [O] at.%, and <1.0 at.% [Cl] (under the detection limit). The deposited silicon nitride has a leakage current density as low as approximately 12.0±0.2 nA/cm^2 and a break down field as high as 12.8±0.2 MV/cm.

Ovanesyan *et al*. and Meng et al. suggested that HCDS reacts with $-NH_2$ groups on the surface and leaves $-NH-$ groups as the primary form of hydrogen bonds in SiN_x.[1,2] *in-situ* FTIR is used to investigate the different surface reaction pathways between N_2H_3 and NH_3. Experimental details and results will be presented.

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AF9-5 Importance of XPS Investigations of ALD Grown 2D Materials

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The success of graphene opened a door for a new class of semiconducting 2D transition metal chalcogenide materials (TMDs) displaying unique properties [1]. ALD MoS_2, as TMDs benchmark, has been widely studied for several applications. In parallel, 2D selenide and telluride analogues, i.e. $MoSe_2$ and $MoTe_2$, have also attracted important interest due to intriguing properties, such as a higher electrical conductivity than that of MoS_2 among others [2, 3].

Recently, we have demonstrated the ALD synthesis of both 2D $MoSe_2$ [4-7] and 2D $MoTe_2$ [8] (using an in-house synthesized precursors), as well as their outstanding performances in different applications. XPS turned a key tool to provide detailed chemical composition analysis of as-deposited 2D Mo TMDs family on different nature substrates. Besides, the post-performance XPS characterization was appealing since the applications of the aforementioned 2D materials involved chemical and/or electronic processes on the surface and it enabled to identify potential chemical composition changes and physicochemical photo-electro stability of the 2D TMDs. This presentation will thus focus on the XPS as key tool for assessment of chemical composition of both as-deposited and post-performance 2D Mo TMDs family, recent experimental results as well as the description of some inherent drawbacks that XPS must face during the analysis of the 2D materials.

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AF9-6 Microstructure and Mechanical Properties of Atomic Layer Deposited Alumina Doped Zirconia

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ZrO_2 metastable polymorphs possess higher hardness and elastic modulus compared to the monoclinic phase that could increase the mechanical endurance of the material [1-2]. Metastable phases of ZrO_2 could be obtained at ambient conditions with a low film thickness or by doping with foreign metal oxides [3-4]. Atomic layer deposited ZrO_2 thin films with high mechanical resilience could be applied as protective coatings.

In the present study, Al_2O_3-doped ZrO_2 films were atomic layer deposited on TiN/Si substrate at 300°C with $ZrCl_4$, $Al(CH_3)_3$ and H_2O. One $Al(CH_3)_3$ + H_2O cycle was performed between every 2, 4, 9, 14 and 19 consecutive cycles of $ZrCl_4$ + H_2O. The thickness of the films neared 100 nm.

Grazing incidence X-ray diffraction revealed that the film grown using ZrO_2: Al_2O_3 cycle ratio of 19:1 was crystallized in its tetragonal polymorph (Fig. 1). Increasing the Al_2O_3 content with cycle ratios of 14:1 and 9:1 stabilized the cubic polymorph. The films with higher Al_2O_3 contents remained amorphous and the reference ZrO_2 films was monoclinic. All the crystalline films possessed a preferential grain orientation to different extent beneath the surface and in the vicinity of the substrate.

Nanoindentation was used to determine the hardness and elastic modulus averaged over 30 indents in each film (Fig. 2). The most rigid films with hardness up to 15 GPa and elastic modulus above 167 GPa were obtained with cubic ZrO_2 stabilized with Al_2O_3. In general, the hardness and elastic modulus increased in the vicinity of the substrate even though the substrate possessed lower values of hardness (12 GPa) and elastic modulus (147 GPa). The texture in thin films had an effect on the mechanical properties.

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AF9-7 Friction and Wear Properties of Low-Temperature Metal Oxides, ***Oili Ylivaara**, L. Kilpi,* VTT Technical Research Centre of Finland*; R. Ritasalo,* Picosun Oy, Finland*; H. Ronkainen,* VTT Technical Research Centre of Finland

In microelectromechanical system (MEMS) devices, thin film made by atomic layer deposition (ALD) can be used as a functional material or as a protective coating due to its ability to coat high-topology surfaces with good conformality. In MEMS devices, there are moving parts involved and during its lifetime, device might be exposed to internal friction causing wear, and long-term reliability issues. Here, we studied low-temperature thin films made by ALD in a system where a silicon counterpart is sliding against ALD coating. Thin films were grown in a temperature range from 85 to 200 °C with a target thickness of 100 nm. Studied materials were Al_2O_3, TiO_2, Ta_2O_5, SiO_2, and some of their nanolaminates. Friction and wear properties of ALD coatings were evaluated with reciprocating sliding test using Anton Paar Tritec Pin-On-Disc tribometer. The load and sliding speed were kept constant during the testing, at 0.3 N and 0.01 m/s, respectively. Sliding distance was up to 20 meters using 10 mm back and forth movement. For each material, friction coefficient was measured during the testing, and after the testing wear surfaces on both the ALD coated silicon sample and silicon pin were analysed, and wear rate was calculated. On most coatings, friction coefficients were on the same level as with reference silicon. In case of the Al_2O_3 and TiO_2 visible tribolayer was formed in the wear surface. In the case of Ta_2O_5, besides tribolayer formation, coating was worn during the testing revealing silicon substrate. For SiO_2 both coating was worn and tribolayer was formed on the surface. Friction and wear results presented here give interesting options for low-temperature protection of the wear surfaces.

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AF9-8 Cryo-ePDF to Measure the Atomic Structure of Amorphous ALD Interfaces, ***Matthias Young**, N. Paranamana, X. He, T. White,* University of Missouri-Columbia

Atomic layer deposition (ALD) provides uniform and conformal thin films that are of interest for a range of applications. To better understand the properties of amorphous ALD films and ALD-modified interfaces, we need improved understanding of their local atomic structure. Previous work demonstrated measurement of how the local atomic structure of ALD-grown aluminum oxide (AlO_x) evolves in operando during growth by employing synchrotron high energy X-ray diffraction (HE-XRD). In this work, we report on efforts to employ electron diffraction pair distribution function (ePDF) measurements using more broadly available transmission electron microscope (TEM) instrumentation to study the atomic structure of amorphous ALD-AlO_x and ALD-modified interfaces. We observe electron beam damage in ALD-coated samples during ePDF at ambient temperature and successfully mitigate this beam damage using ePDF at cryogenic temperatures (cryo-ePDF). We examine both wide-area electron diffraction over a ~200 nm spot size, as well as local diffraction over a <2 nm spot size using cryo-ePDF. The smaller spot size (achieved using convergent electron diffraction with a small convergence angle) allows for local electron diffraction, for example at multiple positions along the cross-section of a 10 nm thick ALD film, and enables characterization of the interfacial atomic structure of the ALD film relative to the bulk structure. We employ Reverse Monte Carlo (RMC) modeling to obtain structural models from the cryo-ePDF data. From these model structures, we derive structural metrics including stoichiometry, pair distances, and coordination environments in the ALD films and ALD-modified interfaces. The cryo-ePDF technique can be used for routine measurement of atomic structure with high spatial resolution to improve understanding of ALD materials, establish structure-property relationships, and help accelerate the timescale for the application of ALD to address technological needs.

AF9-11 Growth and Characterization of Sodium Fluoride Thin Films Deposited by Atomic Layer Deposition, ***Sara Kuraitis**,* Boise State University*; D. Kang, A. Mane, H. Zhou,* Argonne National Laboratory*; J. Soares,* Boise State University*; J. Elam,* Argonne National Laboratory*; E. Graugnard,* Boise State University

Control over the interface between electrolytes and electrodes is key to improving the performance of lithium and sodium ion batteries. Atomic layer deposition (ALD) has attracted interest as a promising approach to the deposition of conformal, pinhole-free thin films on anodes and cathodes in rechargeable battery systems. Such coatings must be stable, prevent dendrite formation, allow for ion conduction, and, ideally, extend cyclability and lifetime. ALD of LiF has shown promise for Li-ion battery systems, and here we report an ALD process for sodium fluoride (NaF) thin films using a similar chemistry. NaF growth experiments were carried out using sodium *tert*-butoxide and HF-pyridine temperatures between 175 and 250 °C. The resulting cubic polycrystalline NaF films exhibited nearly stoichiometric composition (Na:F = 1:1.05), low roughness (Rq ≈ 1.6 nm for ~8.5 nm thick films), and a growth per cycle value of 0.85 Å/cycle on SiO_2 substrates and 3.2 Å/cycle on Al_2O_3. Application of conformal ALD NaF films to battery electrodes may hold promise for improved performance in rechargeable battery systems.

AF9-14 Advanced Applications of Noncontact Electrical Metrology for ALD Films and Interfaces, ***Marshall Wilson**, D. Marinskiy, J. Lagowski,* Semilab SDI

The noncontact charge-based metrology adopted from the silicon industry enables wafer level, very precise electrical characterization without fabrication of any test devices or contaminating contacts. The key advantages are the low cost and rapid feedback that shall benefit the novel implementations of ALD films.

Two different, new applications presently discussed include: 1. characterization of Al_2O_3 and AlN films on wide bandgap AlGaN and GaN structures for HEMT technology; and 2. a unique charge-induced, noncontact ferroelectric poling and characterization of ALD HfO_2 on silicon.

Noncontact metrology employs precise dosing of charge, ΔQ_C, on ALD film surface, performed with a corona discharge in air.The surface charge provides an electrical bias in analogy to gate bias. The response is monitored as a change of the surface voltage, ΔV, measured with a noncontact Kelvin probe. The differential capacitance $C=\Delta Q_C/\Delta V$ is determined, and corresponding C-V and C-Q characteristics provide a means for extraction of parameters characterizing ALD films, and the film/substrate interfaces, including 2DEG. Results are presented for a skew of thermal ALD AlN films with varying ALD cycles on standard, normally on AlGaN/GaN HEMT structures.

The metrology also includes high charge, time resolved SASS voltage technique for direct determination of a dielectric film thickness. For the AlN skew a linear thickness dependence is seen above 50 cycles. However, the growth is slower for 20 cycles. The latter may be an indication of the growth incubation effect analogous to thermal ALD AlN on silicon substrates. ALD films in the HEMT multi-layer structure may be difficult to model in ellipsometry measurements. The direct SASS technique offers an advantage.

For noncontact measurement of ferroelectric Si doped HfO_2, it is critical that the high charge density SASS pulses provide a noncontact means for poling of the film. A subsequent small charge incremental capacitance measurement gives hysteresis characteristics and “butterfly” permittivity curve. In recently introduced metrology, the ferroelectric poling-measuring sequence is fully automated. As demonstrated by results for 4% Si doped ALD HfO_2, such measurement gives the ferroelectric characteristics and the ferroelectric parameters that also includes the maximum capacitance and polarization charge.

The wafer testing includes initial surface voltage mapping. This high speed, 2 min per wafer screening, is a powerful means for evaluation of wafer uniformity after ALD growth.

AF9-17 Assessing the Quality of 3D-printed ALD Films by Low Energy Ion Scattering, ***Philipp Brüner,*** IONTOF GmbH, Germany; *I. Kundatra, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark; *J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany; *T. Grehl,* IONTOF GmbH, Germany

Miniaturizing a spatial ALD reactor for integration into a small print head enables 3D-printing of ALD films in arbitrary patterns on large areas of many cm² by lateral movement of the substrate. The lateral resolution, or line size, of 400 µm is given by the size of the print head, while the vertical resolution is determined by the ALD process employed, ideally reaching atomic layer resolution [1].

In this study, we use Low Energy Ion Scattering (LEIS) to assess the quality and the properties of the deposited films. With its high surface sensitivity of just a single monolayer, the ability to measure film thickness, and the quantitative determination of the elemental composition, LEIS elucidates the lateral homogeneity of the printing process with regards to film thickness, surface coverage, and film composition. The selectivity of the deposition is another important aspect. Naturally, any printed pattern comprises growth areas and non-growth areas, and the print head must be designed in a way to provide maximum selectivity between these areas. Good detection limits in combination with the high surface sensitivity allow LEIS to pick up trace amounts of deposited material on the non-desired areas, such that the selectivity is determined quantitatively.

The samples analyzed include line patterns for testing purposes, consisting of Pt and TiO_2 films, and the ATLANT 3D company logo printed with Pt (fig. 1). While LEIS is normally used as an averaging technique, with analysis areas of a few mm², this type of sample requires a pixel-resolved analysis by scanning the analysis ion beam. We show how the data obtained is evaluated to address the analytical questions outlined above. The LEIS surface scattering signal shows that the Pt film only reaches full coverage in the thicker parts of the film (fig. 1), which is an indication for the growth of individual particles instead of flat films. Excellent selectivity for the deposition of Pt is found, with a lower bound of at least 100,000 (ratio of material deposited on growth area vs. non-growth area).

Analyzing the sub-surface LEIS signal originating from ion scattering processes below the surface allows determining film thickness up to a few nm in a laterally resolved way. We also show how LEIS distinguishes between different film compositions, in this case pure Pt and PtO_x films.

AF9-20 Resistive Switching Performance of Mixed Al_2O_3 and ZrO_2 Thin Films, ***Joonas Merisalu,*** *T. Jõgiaas, A. Kasikov, A. Tamm, J. Aarik, K. Kukli,* University of Tartu, Estonia

In the search for resistive switching (RS) media, mixing dielectric materials is widely practiced, taking advantage of versatile possibilities of atomic layer deposition (ALD). There are some studies on RS of ZrO_2 as the host dielectric oxide [1,2], and few papers have reported RS of ALD-grown ZrO_2:Al_2O_3 mixtures [3] or nanolaminates [4]. In the present study, ZrO_2:Al_2O_3 films were grown on TiN bottom electrodes to thicknesses 10–15 nm by ALD using $Al(CH_3)_3$, $ZrCl_4$ and H_2O as precursors at 300 ºC, whereas earlier $AlCl_3$, as a precursor less prone to thermal decomposition has been applied in the processes [3,4]. In the present study, the ZrO_2:Al_2O_3 cycle ratios ranged from 24:1 to 4:1 yielding Al:Zr cation ratios 0.04–0.4. The RS structures with Ti-Au top electrodes demonstrated multiple clockwise bipolar RS with low to high resistivity window over 5 orders of magnitude in the conductivity scale (Fig. 1), clearly exceeding that observed earlier [3,4], while some samples demonstrated multilevel RS (Fig. 1). The forming voltage, though, was rather high ranging from 4 to 6 V. Interestingly the forming took place under positive voltage applied to Ti-Au electrode which is more common for counterclockwise RS. The effects of cycle ratios and sequencing on the crystalline structure, switching polarity and low to high resistivity ratios will be discussed.

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Atomic Layer Etching
Room On Demand - Session ALE1
Plasma and/or Energy-enhanced ALE

ALE1-1 Interpretation of SiO_2 Atomic Layer Etching Based on Plasma Diagnostics, ***Youngseok Lee,*** *C. Cho,* Chungnam National University, Korea (Republic of); *S. Kim,* Nanotech, Korea (Republic of); *J. Lee, I. Seong, S. You,* Chungnam National University, Korea (Republic of)

Atomic-scale etching in semiconductor processing requires self-limiting behaviors to obtain highly precise controllability of material thickness. Achieving the self-limiting behaviors during atomic layer etching (ALE) is dominantly determined by the processing plasma parameters such as electron density and ion energy distribution, which governs the processing conditions. Knowing such fundamental parameters of the processing plasma is therefore essential in realizing ideal ALE. We analyzed our ALE data obtained by an in situ ellipsometer based on plasma diagnostics using an emissive probe and quadrupole mass spectrometer. What we focused on among various plasma parameters is plasma potential and radical density since they are directly related to ion bombarding energy and chemical reaction during the ALE process, respectively. The analysis explained how the ALE results changed according to processing condition variations. In this presentation, the validity of our plasma diagnostics and the analysis results will be discussed in detail.

Atomic Layer Etching
Room On Demand - Session ALE12
Atomic Layer Etching Poster Session

ALE12-1 On the Reactivity of SiN Surfaces Damaged by Ion Bombardment Towards CH_3F and CF_4 Precursors, ***Erik Cheng,*** *G. Hwang,* University of Texas at Austin; *P. Ventzek, Z. Chen,* Tokyo Electron America

Our recent studies based on extensive first-principles based simulations have revealed that a quasi-equilibrated surface of silicon nitride (SiN) under Ar^+ ion bombardment may consist of a large density of surface defects with lower coordination and that the damaged surfaces tend to be dominated by Si-containing moieties. Contrary to conventional intuition, we have found that these damaged surfaces may be far less reactive than expected towards precursor molecules under typical ALE conditions. From density-functional tight-binding molecular dynamics (DFTBMD), we have observed nearly none of the spontaneous reactions generally expected to happen on these highly damaged surfaces with coordination defects. First-principles calculations reveal that the presence of undercoordinated sites may not imply the presence of dangling bonds, as it is possible for lone pairs and multiple bonds to be present at coordination defect sites. Furthermore, this effect can be further enhanced by overcoordination of atoms within the bulk, which can result in a higher charge density near the surface. When surface reactions are induced under Ar^+ bombardment, far more Si-C bonds are produced than generally expected, while C-N and Si-F bonds are formed relatively infrequently. These findings lead us to speculate that the reactions induced by Ar^+ bombardment may be the key contributor towards the ALE effects seen in experiment and undergo pathways far from what is generally expected given typical chemical intuition.

ALE12-2 Mechanism of Thermal Dry Etching of Metallic Iron Thin Films Using Chlorine and Acetylacetone (acacH), ***Mahsa Konh,*** *A. Teplyakov, A. Janotti,* University of Delaware

Thermal dry etching of metallic Iron thin films using Cl_2 and acetylacetone (acacH) was investigated. Iron metal is commonly used in magnetic random-access memory (MRAM) technology. The etching pathway was followed by detecting expected desorbing fragments during a heating ramp via temperature-programmed desorption (TPD) technique. The chemical properties of the etched surfaces were then analyzed with ex situ X-ray photoelectron spectroscopy (XPS). The morphology of the surface was studied with microscopic techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). To desorb volatile etch products, having an oxidized or halogenated Iron surfaces is vital, since clean surfaces resulted in decomposition of the diketone ligands. The pre-chlorination of the surfaces was shown to lead to the formation of transition metals-containing products at lower temperature compared to those on oxidized surfaces. However, halogenation makes the mechanism more complicated, and the etch product can contain both Fe^{2+} and Fe^{3+}. These products may have a combination of ligands, and their general formula can be expressed as $Fe(acac)_xCl_y$. To corroborate surface reaction mechanisms, density functional theory calculations with periodic slab geometries were performed using the Vienna Ab initio Simulation Package (VASP). Based on the computational investigations, it was concluded that the removal of iron is determined by the nature of the surface-bound acac ligand, favoring the process involving a monodentate configuration. Computational work also illustrated the effect of surface smoothing observed experimentally.

ALE12-3 Atomic Layer Etching of Titanium Nitride With O_2 Plasma and CF_3I Plasma*, **Seon Yong Kim**, Hanyang University, Korea (Republic of); S. Shin, I. Park, J. Ahn, Hanyang University, Korea*

Atomic layer etching (ALE) is a promising etching technology based on sequential, self-limiting surface reactions. Recently, the ALE of conducting transition metal nitrides such as TiN, VN, and TaN has been widely researched. The thermal ALE process of TiN with O_3 and HF gas was reported.[1] However, the speed of process (etched thickness per cycle (EPC) = 0.02 nm/cycle) was too slow to be commercialized. The rapid ALE (EPC = 0.6 nm/cycle) process was reported by using CHF_3 and O_2 down-stream plasma[2], but the process was environmentally problematic because of the high global warming potential of CHF_3 (GWP_{100} = 12,400).

In this work, plasma-based TiN ALE was demonstrated byusing O_2 plasma and non-global warming gas of CF_3I (GWP_{100} = 0.3) plasma. All the processes were carried out at temperature of 35 ℃. In the ALE process, a cycle consists of two steps; oxidation and subsequent removal steps. In the first oxidation step, the O_2 plasma oxidizes the surface of the TiN film.Since the surface is oxidized with O_2 plasma, there are much oxidation state of Ti of +4. This Ti state easily makes the film volatile with the form of TiF_4 for the next steps, instead of non-volatile material of TiF_3. In the second etching step, the oxidized surface of TiN film reacts with F radical in CF_3I plasma. Thenthe oxidized TiN surficial layer is completely removed through a volatile byproduct of TiF_4.

The thickness change was analyzed by spectroscopic ellipsometry and transmission electron microscopy. Also, X-ray photoelectron spectroscopy was used to analyze the TiN surface step by step, after the first oxidation step with O_2 plasma and the second removal step of oxidized surface with CF_3I plasma. Saturation characteristics of EPC were observed in ALE process. The EPC of 0.3 nm/cycle was saturated after sufficient supply of both reactive plasma. Furthermore, the EPC was modulated from 0.15 nm/cycle to 0.3 nm/cycle, which is acceptable for the precise layer control at etching process, by only changing the O_2 plasma source power.

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ALE12-6 Thermal Atomic Layer Etching of Cobalt with Cl_2 Plasma and Hexafluoroacetylacetone (hfacH)*, **Yongjae Kim**, D. Shim, J. Kim, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

As the device dimensions continue to shrink, the back end of line (BEOL) interconnects line must also shrink. [1] Copper was used as a material for interconnect lines, but as the line width narrows, resistance increases rapidly due to surface scattering of electrons. [2] In recent studies, cobalt has been used as a substitute for W in local interconnects. As an alternative metal, cobalt has a greater bulk resistance than copper, but does not require a thick barrier/liner and has less resistance than copper as the line critical dimension decreases. [3] Cobalt deposition based on atomic layer deposition requires an ALE process because the surface roughness increases as the thickness increases. [4] In this work, cyclic thermal atomic layer etching process was performed for cobalt in an inductively coupled plasma (ICP) reactor. The process consists of two steps: surface modification with chlorine plasma and removal with lamp heating. In the first step, the surface of cobalt is modified with a layer of $CoCl_2$ using chlorine plasma. In the second step, the modified surface is removed by thermal desorption with hexafluoroacetylacetone. Etch rate were compared at various conditions of flow rate, plasma power and plasma time. The thickness of the cobalt film was confirmed by cross-sectional SEM imaging, and the roughness of the surface was observed by AFM. The etch rate could be controlled below 1 nm/cycle. Surface roughness was compared according to chlorine plasma power and desorption temperature.

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Keywords: Thermal atomic layer etching, Metal etching, Surface roughness

Atomic Layer Etching
Room On Demand - Session ALE2
Gas-phase and/or Thermal ALE

ALE2-1 Anomalous Etch Behavior of NHC-Containing Gold Precursor*, **Eden Goodwin**,* Carleton University, Canada*; M. Griffiths,* Wayne State University, Canada*; A. Kadri,* McMaster University, Canada*; S. Barry,* Carleton University, Canada

N-Heterocyclic carbenes (NHCs) have been shown to reconstruct gold surfaces by dislocation and displacement of individual atoms on the surface (Amirjalayer, Bakker, Freitag, Glorius, & Fuchs, 2020). When NHCs are used as ligands for gold precursors, the role of NHC could be two-fold; they saturate surface sites and promote self limiting growth like phosphines (Van Daele et al., 2020) or they could abstract gold atoms and reorganize or etch the film.

In this work we analyze the surface behaviour of a newly reported NHC-containing gold precursor – 1,3-diisopropylimidazol-2-ylidene)methylgold(I) – on a gold coated quartz crystal microbalance (QCM). For a 100-cycle pulse sequence (60s pulse, 20s N_2 purge). In situ QCM data demonstrates frequency growth that begins at a rate of 19.6Hz/cycle, gradually decreases to 2.0Hz/cycle, and has an overall rate of 3.9 Hz/cycle (Figure 1). This figure demonstrates the stepwise etch, where the frequency increases during the precursor pulse and plateaus during the purge. Based on the QCM crystals intrinsic mass to frequency ratio of 17.7ng/cm$^{-2}\cdot$Hz, we observe an initial etch rate of 8.9 Au atoms/nm$^{2}\cdot$cycle, a final rate of 1.1 Au atoms/nm$^{2}\cdot$cycle, and an overall rate of 2.1 Au atoms/nm$^{2}\cdot$cycle (compared to 13 atoms/nm^2 in a gold closest packed layer).

Etched QCM crystals were analyzed by atomic force microscopy (AFM) and compared against a standard. The QCM standard had a root mean square roughness of 1.42 nm, while an etched crystal had an enhanced roughness of 2.04 nm. The presence of NHCs on the surface was confirmed by energy dispersive X-Ray analysis (EDX). Changes in surface morphology were also apparent by scanning electron microscopy.

The magnitude of mass loss and its dependence on the presence of the NHC-containing gold precursor, combined with the increased roughness of the surface suggests that surface NHCs induce gold mobility leading to surface reorganization and mass loss of newly-formed gold-containing species. The precursor-surface interaction will be discussed, and in situ mass spectrometry will be shown to support potential surface mechanisms of this precursor.

ALE2-2 Thermal Cyclic Etching of Non-Volatile Material by Self-Stabilizing Organometallic Complex Formation*, **Yoshihide Yamaguchi**, S. Fujisaki, K. Shinoda,* Hitachi, Japan*; K. Sato, M. Izawa,* Hitachi High Technologies, Japan

Remarkable progress on the thermal cyclic etching of non-volatile materials has been made in recent years. The typical procedure for thermal cyclic etching of non-volatile materials such as HfO_2 is cyclic repetitions of formation and desorption of the organometallic complex at a constant temperature [1]. The key steps in thermal cyclic etching is the formation and the desorption of the volatile organometallic complex layer on the surface. The organometallic layer will prevent the diffusion of etching species into the deep at the formation step and it must be easily removed at the desorption step. Our previous study on the thermal cyclic etching of La_2O_3 reported that thermal instability of the corresponding organo-lanthanum complexes must be suppressed in the essential presence of a stabilizer material [2]. In the current study, we present a novel thermal cyclic etching of non-volatile material via a self-stabilizing organometallic complex formation without any additional stabilizer.

The experimental apparatus we used is a tool for thermal gas phase cyclic etching equipped with a single liquid source vaporizer. A La_2O_3 thin film sputtering deposited on a SiO_2/Si wafer was used as a sample. In the first step, the La_2O_3 film was exposed to the vapor of a non-diketonate ligand liquid as the etchant that had a self-stabilizing moiety in the molecule. The sample was then annealed up to 350°C to remove the corresponding organo-lanthanum complex layer from the surface. After consecutive processes of complex formation and its desorption, the La_2O_3 film thickness remaining on the sample surface was evaluated using ellipsometric measurements.

The results showed that the cumulative etched thickness of La_2O_3 film increased linearly in proportion to the number of cycles and that no additional stabilizer was needed. The etching selectivity of La_2O_3 to some other oxides was also confirmed.

From these findings, we conclude that a novel thermal cyclic etching of La_2O_3 by self-stabilizing organometallic complex formation without an additional stabilizer has been successfully demonstrated.

[1] Y. Lee et al., Journal of Vacuum Science & Technology A 36, 061504 (2018).

[2] Y. Yamaguchi et al., ALE workshop AP+PS+TF-ThM1 (2019).

Atomic Layer Etching
Room On Demand - Session ALE3
Solution-based including Wet ALE

ALE3-1 Novel Electrochemical Concepts for Enabling Atomic Layer Etching of Metals, *Y. Gong, **Theodore Phung**, R. Akolkar,* Case Western Reserve University

In this talk, we will outline electrochemical concepts for achieving atomic layer-by-layer etching of interconnect materials such as copper and ruthenium used in semiconductor devices. By employing a two-step process comprising surface-limited electrochemical oxidation followed by selective etching of the surface oxide monolayer, we will demonstrate the atomic layer etching (electrochemical ALE) of copper and ruthenium. Characteristics of the electrochemical ALE process steps will be outlined using a suite of in situ and ex situ techniques including electrochemical measurements, quartz crystal micro-gravimetry, and high-resolution TEM or AFM. Finally, the critical role of the electrode potential in enabling layer-by-layer etching without surface roughness amplification will be highlighted. Underlying electrochemical mechanisms and thermodynamic considerations will be explained leading to guidelines for optimal electrochemical ALE process design.

Atomic Layer Etching
Room On Demand - Session ALE8
Integration of ALD + ALE

ALE8-1 Simultaneous Selective Deposition and Etching of Ru for Atomic Layer Processing of SiO_2, ***Sumaira Yasmeen**, B. Ko, B. Gu, H. Lee,* Incheon National University, Korea (Republic of)

Nanofabrication is facing multiple challenges, such as patterning limits and transition to 3D structures, with the downscaling of devices to sub-5nm scale. To overcome the existing challenges, area-selective atomic layer deposition (AS-ALD) has surfaced as a promising candidate for a toolbox of nanofabrication. In our previous work, we introduced a Si precursor type inhibitor using bis(methylamino)dimethylsilane (DMADMS) and it showed reliable AS-ALD with high process compatibility with current unit processes of nanofabrication. In this work, the AS-ALD is extended to a multipurpose process that DMADMS is used as a Si inhibitor as well as precursor for SiO_2 ALD using ozone as an oxidant. In addition, AS-ALD Ru process is also integrated into the SiO_2 process as a supporting layer for oxidation protection and lateral growth control. In a detailed process, the experiments are designed in such a way that DMADMS inhibitor is first adsorbed selectively on SiO_2 surface. After DMADMS inhibitor adsorption, Ru AS-ALD process is carried out and Ru is selectively deposited on Cu surface only, given that DMADMS can efficiently block Ru ALD. In the following process, SiO_2 AS-ALD process is performed by oxidizing DMADMS inhibitor by ozone counter reactant. A SiO_2 film nucleates solely on SiO_2 surface, while ozone etches out the AS-ALD Ru from the Cu surface simultaneously. In this way, self-aligned nanopatterns can be formed without additional plasma dry etching processes and photolithography. This combined atomic layer processing is believed to be an example to show effective integration and applicability of AS-ALD into the current nanofabrication technology.

ALD for Manufacturing
Room On Demand - Session AM1
Equipment Design/Modeling/Large Format/Precursor Delivery

AM1-1 Closed Loop Control of ALD/ALE Precursor Dose Delivery, ***Jim Ye**, J. Ding, V. Saptari,* MKS Instruments, Inc.

Consistent precursor delivery is needed in ALD/ALE processes for generating a stable and homogenous deposition. Unstable deposition will cause defects and create wafer to wafer and batch to batch variations. Further improvements in ALD/ALE process throughput and cutting the waste of precursors will require a tighter control on precursor dose delivery to the process chamber.

Previously, concepts of ALD/ALE precursor concentration control have been reported. However, there are two potential problems in this approach. First, tuning the concentration of precursor is a relatively slow process which can be accomplished by either varying the temperature of precursor container or adjusting the dilution/carrier gas flow. They do not have enough bandwidth to handle faster varying changes in the flow. The second problem is that a constant concentration will not guarantee a constant dose in each precursor pulse due to other factors such as a switch drift.

In this work, we present a concept solution involving a gas sensor and a pulse MFC. The gas sensor measures the precursor concentration out of the source in real time and feeds the readings to a pulsed MFC immediately downstream to the sensor. The pulse MFC generates ALD/ALE precursor pulses. It continuously adjusts the total flow rate (pulse height) or pulse duration for each precursor pulse to achieve a constant dose of the precursor to the processing chamber.

AM1-2 Efficiency Characterization of Reactor-Scale Gas Exchange by CFD, ***Anton Persson**,* Linköping University, Sweden*; Ö. Danielsson,* Physicomp AB, Sweden*; H. Pedersen, M. Karlsson,* Linköping University, Sweden

To utilize the sequential surface chemical reactions essential to ALD processes, the gas mixture in the ALD reactor needs to be exchanged between the metal precursor pulse and reagent pulse. This is commonly done through a continuous flow of carrier gas (purge) between the pulses and is often vital for a successful ALD process. Insufficient exchange can lead to unintentional reactions, which in turn may cause poor film thickness uniformity or formation of structural defects. In contrast, excessive purging leads to prolonged process times and waste of carrier gas. While the optimal purge time can be obtained from extensive experimental work, such studies are seldom reported for new ALD processes or fully understood at the full wafer scale, and is reactor design specific. ALD process development therefore has a lot to gain from a simple, yet powerful modelling approach to study gas transport at the reactor scale.

This work implements methods common in e.g. ventilation modeling to investigate efficiency aspects in gas exchange. An ALD reactor for 200 mm substrates with six in-plane, symmetrically positioned gas channels was modelled using computational fluid dynamics (CFD). It was assumed that the precursor partial pressure is small in relation to the partial pressure of the carrier gas, such that changes in the overall velocity field between pulse and purge steps may be neglected. Several configurations were tested, where precursor and reagent entered from opposing or asymmetric directions, with different carrier gas flow rates equivalent to N2 in a range of 50-200 sccm per inlet.

Purge times were quantified by the residence time distribution (RTD). It was shown that RTD was primarily a function of total mass flow rate and reactor geometry, and less affected by pulse time.

Moreover, precursor usage efficiency was characterized by the local mean age (LMA) measure, which represents the mean time for a particle to reach a certain location in the reactor in a steady state situation, calculated from the inlet. It was seen that the constant carrier gas flow in some configurations caused “blocking effects”, obstructing the precursor to spread uniformly over the substrate. Thus, care should be taken to engineer the flow field for efficient precursor usage.

While the model is subject to simplifications, the general trends and relative performance among test cases are expected to be accurate. Once the main design frame is established, promising configurations could be analyzed further by extending the model, e.g. by taking reversible adsorption on reactor walls into account.

ALD for Manufacturing
Room On Demand - Session AM2
Spatial/R2R/Fast ALD

AM2-1 Surface Modification and Stabilization of Photoluminescence Perovskite Nanocrystals via Atomic Layer Deposition*, Y. Jing,* Huazhong University of Science and Technology, China*; K. Cao,* ***Rong Chen,*** State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

Photoluminescence perovskite nanocrystals (NCs) have shown significant potential in optoelectronic applications in view of their narrow band emission with high photoluminescence quantum yields (PLQYs) and color tunability. However, their poor stability in light, heat and water environments still hinders practical applications in optoelectronic and bioimaging fields due to their ionic character. Atomic layer deposition (ALD) has been developed as an attractive method to stabilize the crystal structure of perovskite NCs through encapsulation and surface passivation. In this presentation, several stabilization methods through ALD are introduced. First, a low-temperature Al2O3 ALD process was developed to enhance the stability of CsPbBr3 quantum dots-silica sphere in light, water and heat, which originated from the crystal structure stabilization after ALD coating. Nonetheless, a significant photoluminescence (PL) quenching of NCs was typically observed upon Al2O3 ALD. Accordingly, a specially designed ALD reactor integrated a FTIR spectrometer was exploited, which enabled in-situ characterizations to investigate ligands exchange and evolution during deposition after each precursor dosing. It was found that the surface chemical reaction between ALD precursor and capping oleic acid (OA) ligands led to reorganization of OA ligands that increased surface trap sites, leading to PL quenching. Based on the reaction mechanisms observed, a hybrid passivation strategy was developed to simultaneously enhance the photoluminescence quantum yield and the stability of perovskite NCs by two-step modification with surface halogen replenishment and ALD. Consequently, the PL quenching was avoided and the perovskite NCs/Al2O3 nanocomposites exhibited exceptional stability against water, light and heat. Our work provides a versatile method for preparing ultrastable perovskite NCs through ALD method and significantly improves their potential in LED illumination and backlight displays.

AM2-4 Influence of Reactor and Pattern Geometry on Atomic Layer 3D Printing*,* ***Ivan Kundrata,*** *M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann, M. Barr, S. Tymek,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany*; P. Brüner,* IONTOF GmbH, Germany

As additive manufacturing in its various forms is shifting the paradigm of traditional manufacturing, the same space opens in the field of thin film deposition. Atomic layer deposition is, due to its inherent separation of reactions, uniquely suitable for adaptation into a 3D printer. In fact, the concept of spatial atomic layer deposition, which can be considered as a precursor for 3D atomic layer printing, goes all the way back to 1974.[1] Despite the many challenges of creation and miniaturization of spatial ALD reactors, atomic layer 3D printing was successfully proved as a concept recently.[2,3]

However, for the best performance of atomic layer 3D printing, the influence of geometry of both the reactor and the pattern being printed has to be examined. Generally, due to the necessary spatial separation of precursor and reactant, edge effects are necessarily present. Moreover, deviations from the perfect printing geometry cause additional line edge effects and selectivity defects.

In this study, we created a general theoretical model of effects caused by spatial separation on the printed pattern. The theoretical model was then confronted with experiments performed on the atomic layer 3D printer developed by ATLANT 3D Nanosystems.

The theoretical effects and samples analyzed include edges of lines, overlaps of lines including rastering and gradients, multiple paths overlaps during pattern printing and step pattern printing. To prove that these effects are independent of the specific material, the effects are explored for TiO$_2$, ZnO, and Pt.

[1] Tuomo Suntola, Jorma Antson.Method for producing compound thin films. US4058430A,United States Patent and Trademark Office, 29 November 1974.

[2] Ivan Kundrata, Maksym Plakhotnyuk, Maïssa K. S. Barr, Sarah Tymek, Karol Fröhlich, Julien Bachmann (2020, June 30) An Atomic-Layer 3D Printer [Conference presentation] ALD/ALE 2020

[3] Cesar Arturo Masse de la Huerta, Viet H. Nguyen, Abderrahime Sekkat, Chiara Crivello, Fidel Toldra-Reig, Pedro Veiga, Carmen Jimenez, Serge Quessada, David Muñoz-Rojas.Facile patterning of functional materials via gas-phase 3D printing [2020, Cornell University Condensed Matter, Materials Science]

AM2-7 Realization and Dual Angle In-situ OES Characterization of Saturated 10-100 ms Precursor Pulses in a 300 mm CCP Chamber Employing de Laval Nozzle Ring Injector for Fast ALD*,* ***Abhishekkumar Thakur,*** *S. Wege, S. Bürzele, E. Ricken,* Plasway Technologies GmbH, Germany*; M. Krug,* Fraunhofer IKTS, Germany*; J. Sundqvist,* BALD Engineering AB, Sweden

ALD-based spacer-defined multiple patterning schemes have been the key processes to continued chip scaling, and they require PEALD or catalytic ALD for low temperature and conformal deposition of spacers (typically SiO$_2$) on photoresist features for the subsequent etch-based pitch splitting. Other SiO$_2$ applications in the logic and the memory segments include gap fill, hard masks, mold oxides, low-k oxides, hermetic encapsulation, gate dielectric, inter-poly dielectric ONO stack, sacrificial oxide, optical films, and many more. ALD is limited by low throughput that can be improved by raising the growth per cycle (GPC), using new ALD precursors, performing batch ALD or fast Spatial ALD, shrinking the ALD cycle length, or omitting purge steps to attain the shortest possible ALD cycle. Today’s latest and highly productive platforms facilitate very fast wafer transport in and out of the ALD chambers. Current 300 mm ALD chambers for high volume manufacturing are mainly top-down or cross-flow single wafer chambers, vertical batch furnaces, or spatial ALD chambers. We have developed a Fast PEALD technology [1], realizing individual precursor pulses saturating in the sub-100 ms range. The key feature of the technology is the highly uniform, radial injection of the precursors into the process chamber through several de Laval nozzles [2]. To in-situ study (concomitantly from the top and the side of the wafer surface) individual ALD pulses in the 10-100 ms range, we use two fast scanning (≤10 ms acquisition time per spectrum ranging from 200 nm to 800 nm) Optical Emission Spectrometers with a resolution in the range of 0.7 nm. We present the results for PEALD of SiO$_2$ exhibiting substrate surface saturation for 30 ms of BDEAS pulse (Fig. 1) and 50 ms of O$_2$ plasma pulse (Fig. 2). All the processes were carried out in a 300 mm, dual-frequency (2 MHz and 60 MHz) CCP reactor in the temperature range of 20 °C to 120 °C and at ~1 Torr max. pulse pressure. The in-situ, time-resolved OES study of O$_2$ plasma pulse, indicating saturation ofO* (3p^{5}Pà3s^{5}S) emission peak already at 50 ms pulse duration (Fig. 3, 4) and associated extinction of reactive O* within 161 ms (Fig. 5), suggest room for yet faster process. The mean GPC diminishes with the electrostatic chuck temp (Fig. 6). We will present a more optimized PEALD SiO$_2$ process and stacking of Fast PEALD SiO$_2$ on top of Fast PEALD Al$_2$O$_3$ in the same chamber without breaking the vacuum. The results will comprise XPS, TEM, film growth uniformity across 300 mm wafer, and residual stress investigation for the film stack.

Ref.

[1] AVSALD2020, Abstract# 2415, Oral Presentation AM-TuA14

[2] Patent US20200185198A1

ALD for Manufacturing
Room On Demand - Session AM4
ALD on Particles

AM4-1 Improvement of Mechanical Properties of Nanoparticles-Based Thin Films by Using Atomic Layer Deposition*, **Fatma Trabelsi**, M. Fivel ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France*; R. Salhi,* Laboratory of Advanced Materials, National School of Engineers of Sfax, University of Sfax, Tunisia*; F. Mercier, E. Blanquet ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France

Nanoparticle-based thin films are gaining interest in recent decades for catalysis, electronic or optical applications. However, their poor mechanical reliability and durability limit their industrial and commercial applications.

In this work, we report on a low temperature hybrid synthesis approach to insure the durability and encapsulation of photonic conversion films for its further integration in silicon solar cells. The proposed hybrid approach consists first on the synthesis of rare earths (Erbium and Ytterbium) codoped TiO_2 nanoparticles (size ~ 11 nm) fabricated by hydrothermal-assisted sol-gel method. Then, the nanoparticles are dispersed at the surface of silicon substrates using a spin-coating process (film thickness 750-900 nm). Finally, Er^{3+}-Yb^{3+}codoped TiO_2 upconversion nanoparticles in the powder phase are coated with an amorphous Al_2O_3 layer using atomic layer deposition technique (ALD) as a unique approach to reinforce mechanical properties of various photoluminescent nanoparticle porous thin films at a relatively low temperature without drastically changing their original structure.

The impact of different ALD-Al_2O_3 thicknesses and forming gas annealing step on the structural, compositional and mechanical properties ofEr^{3+}-Yb^{3+} codoped TiO_2 nanoparticles assembled on n-type Si (100) substrate are investigated. For that purpose, various analysis approaches involving automated crystal phase and orientation mapping in TEM (ACOM-TEM), scanning transmission electron microscopy–energy-dispersive spectroscopy (STEM-EDS), scratch test and nanoindentation are performed to understand the links between the structural properties and the mechanical properties.

The results indicate a clear increase in the adhesion of nanoparticle thin films to the Si substrate with increasing ALD-Al_2O_3 thickness followed by forming gas annealing treatment. This behavior is a consequence of the infiltration of Al_2O_3 layer within the porous matrix, as a result, effective interparticle bonding and filling of the pores are accomplished.

AM4-2 Three-Dimensional Conformal Coating of Particles *Resting* on a Surface by Vapor-Phase Infiltration*, **Chang-Yong Nam**,* Brookhaven National Laboratory

Three-dimensional (3D) encapsulation of micro- and nanoparticles by atomic layer deposition (ALD) can have broad applications but remains a technical challenge. Current ALD techniques for coating particles employ physical agitation to expose all surfaces of particles to precursors during the deposition process, requiring specialized chambers, such as fluidized bed reactors and rotary chambers and, therefore, only applicable to bulk powders in large volume and quantities. Achieving 3D encapsulation by directly applying conventional ALD on particles resting on a substrate without agitation would allow much smaller volumes and smaller sizes of particles to be used, but the conventional ALD on a particle stationary on a flat substrate yields a coating only on exposed surfaces, not on the bottom side directly in contact with the substrate. Here, we report a novel 3D conformal coating technique for individual particles on all sides while they are resting on an inert polystyrene (PS) film to enable the growth of inorganic films not only on the particle's exposed surfaces, but also on the bottom side that is in contact with the polystyrene [Liapis et al., *Adv. Mater. Interfaces***7**, 2001323 (2020)]. This technique repurposes vapor-phase infiltration (VPI), an organic-inorganic hybridization technique derived from ALD in which vapor-phase inorganic precursors perfuse into a polymer matrix and react with functional groups within it to form organic–inorganic hybrids. We exploit the inert nature of PS to use it as a substrate 'transparent' to vapor-phase ALD precursors. We demonstrate that the conformal coatings of alumina realized by this technique improve the stability in aqueous environments for two optically relevant particles: compound semiconductor laser microdiscs and lead halide perovskite nanocrystals, which have important optical tagging applications for *in vivo* and *in vitro* biomedical imaging.

AM4-5 Atomic Layer Deposition (ALD) of Ultra-Thin Diffusion Barriers on ZnSe Microparticles for Phase Stability in Chalcogenide Glasses for Mid-Infrared Optics*, **Jaynlynn Sosa**,* Nanoscience Technology Center, University of Central Florida*; M. Chazot ,* CREOL, College of Optics and Photonics, University of Central Florida*; C. Feit ,* Department of Materials Science & Engineering, University of Central Florida*; A. Kostogiannes,* Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA*; M. Kang, C. Blanco , K. Richardson,* CREOL, College of Optics and Photonics, University of Central Florida*; P. Banerjee,* Department of Materials Science & Engineering, University of Central Florida

ZnSe embedded chalcogenide glass (ChG) composites are optically active in the mid-infrared (IR) and are ideal for niche applications in medical diagnosis, military missile heat-sensing, and chemical identification. The embedded ZnSe crystals play a critical role in providing lasing activity while the ChG - $As_2S_{3-x}S_{ex}$ matrix, acts as a host that can be drawn into fiber and provides the necessary mid-IR transparency. However, during synthesis, the ZnSe particles are prone to dissolution in the $As_2S_{3-x}S_{ex}$ matrix due to a high temperature (650 C) melting and homogenization process. Here we demonstrate that a thin amorphous barrier layer of Al_2O_3 deposited using atomic layer deposition (ALD) on ZnSe microparticles 5-10 µm in average diameter is successful to prevent ZnSe dissolution in the $As_2S_{3-x}S_{ex}$ matrix even after extended melting and homogenization at 650 C for 8 hours. This talk will highlight some of the key process innovations required to overcome challenges of ALD on powdered components for functionalizing and enhancing performance of multiphasic glasses for optical applications.

Amorphous aluminum oxide (Al_2O_3) was deposited using alternate pulses of trimethyl aluminum and H_2O on 1 gm batch size ZnSe using a customized rotary barrel reactor inside a viscous-flow ALD furnace attached to a quadrupole mass spectrometer (QMS). The temperature of deposition was kept at 180 C and the number of cycles were varied from 100 to 300 cycles. The ZnSe particles were sieved to an average size of 5-10 µm and a maximum size ≤ 20 µm. The coated particles were characterized by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The crystallinity of the ZnSe-$As_2S_{3-x}S_{ex}$ glasses were evaluated using x-ray diffraction (XRD) and their composition stability spatially mapped across individual ZnSe particles embedded in $As_2S_{3-x}S_{ex}$ matrix using Raman microspectroscopy.

Whereas 100 ALD cycles provide partial protection to dissolution for the ZnSe in $As_2S_{3-x}S_{ex}$, a 300 cycle ALD Al_2O_3 on ZnSe particles is sufficient to provide phase and composition stability to the ZnSe embedded $As_2S_{3-x}S_{ex}$ glass. Through our investigation, we exemplify the efficacy and potential of ALD of ZnSe powder in improving the stability of optical materials while still achieving optimal mid-IR lasing and transparency.

ALD for Manufacturing
Room On Demand - Session AM5
ALD for Manufacturing Poster Session

AM5-1 Development of MeCpPtMe3 Platinum Process by Rotary Type Reactor Atomic Layer Deposition on Powders*, **Min Jong Kil**, S. Yoon,* Korea Electronics Technology Institute, Korea (Republic of)*; S. Jung,* Gachon University, Korea (Republic of)*; H. Kim,* Korea Electronics Technology Institute, Korea (Republic of)*; T. Kim,* Gachon University, Korea (Republic of)*; H. Kim,* Korea Electronics Technology Institute, Korea (Republic of)

Atomic layer deposition has been widely studied to deposit materials with optimized usage and conformal coating on various applications such as semiconductor, energy storage/conversion devices, and catalyst. However, conventional atomic layer deposition is not suitable for powders or (nano)particles to coat materials with static processes. Therefore, atomic layer deposition for powders is developed in two types: fluidized bed reactor and rotary type reactor. At first, vertical fluidized bed reactor type atomic layer deposition was developed to conformally coat on (nano)particles. However, to develop the excessive usage of precursors in fluidization method, horizontal rotary type atomic layer deposition is developed to optimize the usage of precursor, especially noble metal precursors. To coat materials by powder atomic layer deposition, optimization of precursors and agglomeration/breakage of powders are required to achieve atomic layer deposition mode. In this study, process optimization and powder agglomeration/breakage are solved using rotary reactor type atomic layer deposition with MeCpPtMe3 platinum precursor and oxygen. For process optimization, each step pulse time is controlled with stop valve mode on silicon wafer. Using this optimized process, powder agglomeration/breakage is achieved by controlling ball type, size, and rotation speed. Platinum process optimization is achieved by X-ray reflectometry for thickness and density. Conformal coating on powders is confirmed by transmission electron microscopy and energy dispersive X-ray spectroscopy. This optimized process is applied to the biomass-derived graphene-based carbon to confirm the performance difference between conventional atomic layer deposition and powder atomic layer deposition. These results are expected to be valuable for atomic layer deposition on nanoparticles.

AM5-2 Nanoscale Film Thickness Gradients Printed in Open Air by Spatially Varying Chemical Vapor Deposition, *Jhi Yong Loke,* University of Waterloo, Canada

Nanoscale films are integral to all modern electronics. To optimize device performance, researchers vary the film thickness by making batches of devices, which is time-consuming and produces experimental artifacts. We present thin films with nanoscale thickness gradients that are rapidly deposited in open air for combinatorial and high-throughput (CHT) studies. Atmospheric pressure spatial atomic layer deposition reactor heads are used to produce spatially varying chemical vapor deposition rates on the order of angstroms per second. We printed ZnO and Al2O3 films with nm-scale thickness gradients in as little as 45 seconds and performed CHT analysis of a MIM diode and perovskite solar cell. By testing 360 Pt/Al2O3/Al diodes with 18 different Al2O3 thicknesses on a single substrate, we identified a thicker insulator layer (6.5 to 7.0 nm) for optimal diode performance than has been reported previously. An Al2O3 thin film encapsulation layer was deposited by atmospheric pressure chemical vapor deposition (AP-CVD) on a perovskite solar cell stack for the first time and a convolutional neural network was developed to analyze the perovskite stability. The rapid nature of AP-CVD enables thicker films to be deposited at a higher temperature than is practical with conventional atomic layer deposition. The CHT analysis showed enhanced stability for 70 nm encapsulation films.

AM5-5 Measurements and Prediction Model for the Evaporation of Bis(diethylamino)silane, *Seung-Ho Seo, E. Shin, Y. Lee, D. Kim, H. Shin,* GO Element, Korea (Republic of); *C. Kim, W. Lee,* Sejong University, Korea (Republic of)

In ALD and CVD processes, the evaporation rate of the precursor affects the growth rate of the thin film. Therefore, a sufficient amount of the precursor must be continuously supplied to the reactor, and it is important to measure and predict the amount of precursor supply in an actual ALD system. The amount of precursor supply varies depending on the structure and temperature distribution of the precursor delivery system including the canister, the type of precursor, and the flow rate of the carrier gas. Recently, a nondispersive infrared (NDIR) gas analyzer was installed in the canister outlet pipe to measure the partial pressure of a Ta precursor, and the evaporation amount of the precursor was calculated [1]. However, in order to accurately predict precursor evaporation, it is necessary to measure the precursor partial pressure and temperature inside the canister.

In the present study, we measured the evaporation amount of a liquid silicon precursor, bis(diethylamino)silane (BDEAS), under various conditions and presents a model to predict the evaporation amount of the precursor. In order to accurately understand the evaporation characteristics, we measured the pressure and the temperature inside the canister were measured, not in the delivery line. We also measured the evaporation amount of BDEAS in real-time using an ultrasonic level sensor installed at the bottom of the canister. To predict the evaporation amount of the liquid precursor, the evaporation coefficient was calculated using the Hertz-Knudsen-Langmuir equation. The predicted evaporation amount of the precursor agreed well with the measurement result. The construction of the precursor evaporation prediction model is expected to be used to optimize the precursor delivery system design and the ALD process condition.

[1] B. A. Sperling et al., J. Vac. Sci. Technol. A 37, 060907 (2019).

AM5-6 Interface Modification of Bismuth by Atomic Layer Deposition: Enhanced Thermoelectrical Performance, *Shiyang He, A. Bahrami, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

Interfaces of phase boundaries play a critical role in the carrier/phonon transport in thermoelectric materials. It remains a big challenge to control over both chemical composition and dimension of interfaces precisely by traditional approaches. Herein, a strategy of interfaces modification based on powder atomic layer deposition (PALD) is introduced to accurately control and modify the phase boundaries of pure Bismuth (Bi). To demonstrate the effect of this strategy, ultrathin layer of Al_2O_3 is uniformly deposited on Bi particles. It is observed that 5 cycles deposition of Al_2O_3 significantly scattered the phonons and 10% reduction on thermal conductivity in Bi-Al_2O_3 system can be achieved. Owing to the carrier scattering in the Bi-Al_2O_3 system, the electrical conductivity decreased from 5700 S/cm to 4500 S/cmfor 5 cycles coated Bi. However, the Seebeck coefficient increases from -69 µV/K to -78 µV/K which results in high power factor. Thanks to the precisely interface modification, a maximum *zT* of 0.13 with 5 cycles deposition of Al_2O_3 at 300 K is obtained, which is 11.2% higher compared with that of pure Bi. As a powerful interfacial modification strategy, PALD-based approach can be extended to other thermoelectric material system simply, which may contribute to the development of high-performance thermoelectric materials.

AM5-9 Low Resistivity Titanium Nitride Thin Film Fabricated by Atomic Layer Deposition on Silicon, *Cheng-Hsuan Kuo,* UC San Diego, Taiwan; *V. Wang, z. zhang, H. Kashyap, A. Kummel,* UC San Diego

Titanium nitride (TiN) thin films areutilized as the diffusion barriers for Co and W metal layers as well as the gate metal barrier in CMOS and memory devices due to their low resistivity and good electrical conductivity. TiN is also used as a coating for hard disk drives[1].Low resistivity TiN has been deposited in commercial devices by plasma enhanced ALD (PEALD) and by physical vapor deposition. However, for high aspect ratio features, deposition by thermal ALD is needed because of the high conformality of the thermal ALD process and for back-end compatible deposition below 350 °C.Previously Wolf *et al.* demonstrated that at 400 °C, ALD of TiN with $TiCl_4$ and N_2H_4 resulted in a film with a resistivity of 500 mohm-cm[2].In this work, it is shown that the resistivity can be decreased below 200 mohm-cm when deposited at 300 °C - 350 °C by reducing the oxygen in the films.

Titanium tetrachloride ($TiCl_4$) and anhydrous hydrazine (Rasirc, Brute Hydrazine$^{\text{Ò}}$) were employed as the precursors with ultra-high purity nitrogen purge gas. To produce low resistivity films, a turbo molecular drag pump (Edwards EPX) was employed to maintain a high compression ratio during ALD pulsing. The TiN ALD chamber was connected to an *in-vacuo* Auger electron spectrometer (RBD Instruments), which was used to determine the atomic composition of ALD TiN after 50 cycles of deposition. Pulse lengths and purge times were optimized at sample temperatures of 300 °C and 350 °C on HF-cleaned Si (100) or degreased SiO_2; the optimized pulse times were 300 ms for $TiCl_4$ and 2400 ms for N_2H_4. Surface morphology was measured by *ex-situ* atomic force microscopy (AFM). To determine resistivity, four-point probe (Ossila) measurements were performed on TiN thin films on degreased SiO_2 substrates. Scanning electron microscopy (SEM), ellipsometry, and X-ray reflectivity (XRR) were used to measure TiN film thicknesses.

AM5-12 Morphology-Controlled MoS_2 by Low-Temperature Atomic Layer Deposition, *Chengxu Shen, M. Raza, P. Amsalem, T. Schultz, N. Koch, N. Pinna,* Humboldt-Universität zu Berlin, Germany

Two-dimensional (2D) transition metal dichalcogenides (TMDs) such as MoS_2 are materials for multifarious applications such as sensing, catalysis, and energy storage.[1] Due to their peculiar charge-transport properties, it is always desired to control their morphologies from vertical nanostructures to horizontal basal-plane oriented smooth layers.[2] Due to the high conformality, atomic layer deposition (ALD) exhibits promising potential in the precise control of the thickness and morphologies of the deposited layers, especially for the preparation of complex nanostructure.[3]

In this work, we established a low-temperature ALD process for MoS_2 deposition using bis(t-butylimino)bis(dimethylamino)molybdenum(VI) and H_2S precursors. Polycrystalline MoS_2 is conformally deposited on carbon nanotubes, Si-wafers, and glass substrates. Moreover, the morphologies of the deposited MoS_2 films are tuned from smooth film to vertically grown flakes, and to nano-dots, by controlling the reaction parameters/conditions and post sulfurization process. Noticeably, the deposited MoS_2 nanostructures show morphology-dependent optical and electrocatalytic properties, allowing us to choose the required morphology for a targeted application.

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Area Selective ALD
Room On Demand - Session AS1
Selective ALD by Area-Activation

AS1-1 Area-Selective Atomic Layer Deposition Patterned by Electrohydrodynamic Jet Printing for Additive Nanomanufacturing of Functional Materials and Devices*, **Tae Cho**, N. Farjam, C. Allemang, C. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. Peterson, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Personalized health care has lead to an increase in demand for customization of integrated nanosystems. However, existing additive nanomanufacturing techniques are often restricted by long processing times and/or strict material requirements. For instance, electrohydrodynamic jet (EHD) printing allows for fast and versatile printing down to 30 nm feature sizes, but requires special attention to the physical/chemical properties of the ink. To expand on this nanoprinting approach, we have demonstrated that by patterning polymer geometries, EHD can be used to locally activate/deactivate ALD growth [1,2].

In this study, we combined area-selective atomic layer deposition (AS-ALD) and EHD to pattern inhibitor polymers with sub-micrometer resolution and high line speeds [2]. This allows patterning of ZnO, Al_2O_3, SnO_2, and their ternary combinations with tunable geometry and elemental composition. With additive EHD printing, polyvinylpyrrolidone was printed with an average linewidth of 312 nm to deactivate the surface to ALD growth. Furthermore, using solvent-based subtractive EHD printing to dissolve polymethylmethacrylate [1], an average linewidth of 9 µm region was patterned to activate the surface.

Using this technique, a bottom-gate, top-contact thin-film transistor, with an on/off current ratio of greater than 10^5,was fabricated using zinc-tin-oxide (ZTO) as the semiconductor and aluminum-doped zinc oxide as the source and drain electrical contacts. We have also demonstrated that by combining thermal and plasma-enhanced ALD processes, ZTO film density can be increased, which resulted in the highest reported μ_{FE} of ~22 $cm^2V^{-1}s^{-1}$ after post-deposition anneal at 400 °C [3]. However, due to the thermal budget of the inhibitor polymers used in AS-ALD–EHD process, a low ALD deposition temperature was used, yielding lower mobility compared to the thermal-plasma ALD device. Therefore, to improve device performance, we have studied the effect of the oxidant (H_2O, O_3, and plasma) and deposition temperature on the ALD selectivity and device performance. This technique can be further used to print on nonplanar and/or flexible substrates, without the need for traditional lithography.

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AS1-2 Surface-Activated Area-Selective Atomic Layer Deposition of Palladium*, **Himamshu Nallan**, X. Yang,* University of Texas at Austin*; B. Coffey,* Lam Research Corporation*; J. Ekerdt,* University of Texas at Austin

Flexible electronics and next-generation roll-to-roll nanomanufacturing rely on the use of polymeric substrates, which constrain processing temperatures. In addition to typically operating a low thermal budget, ALD can provide atomic-level control, making it a suitable method of deposition for these applications. In this work, we present an area-selective ALD (AS-ALD) route to grow difficult-to-nucleate metals that promises to mitigate the need for post-deposition removal of any metal that grows non-selectively.

The area-selective deposition of palladium metal uses palladium(II) hexafluroacetylacetonate and H_2 at low temperature (≤150 °C). There is a significant nucleation delay during the deposition of Pd with these coreactants on various metal-oxide substrates due to the low reactivity of the H_2 molecule with $Pd(hfac)_2$ as well as the Hhfac reaction product inhibiting oxide surface sites. Typically, a high deposition temperature or hydrogen plasma is employed to facilitate Pd film growth. Here we report an alternative route to enhancing palladium deposition and conferring selectivity by employing a pre-patterned metallic seed layer. First, AS-ALD of nickel(II) oxide is carried out on pre-patterned sp^3 carbon-rich resist using bis(N,N'-di-tert-butylacetamidinato)nickel(II) and H_2O as coreactants at 200 ºC to yield conformal, carbon-free oxide films, with high selectivity and no nucleation delay. Subsequently, the nickel(II) oxide films are reduced with atomic and/or molecular hydrogen to nickel(0), which readily facilitates the surface dissociation of H_2 and thereby enhances the deposition of Pd, defining a route to selective deposition. As only surface nickel(0) provides nucleation enhancement for metal-on-metal deposition, partial, superficial reduction of the nickel(II) oxide film is sufficient. In this way, the selectivity of the oxide deposition process is conferred to palladium deposition as well. In-situ x-ray photoelectron spectroscopy is used to determine the presence and oxidation states and film stoichiometry of palladium and nickel. Ex-situ x-ray reflectivity and atomic force microscopy are used to probe the film thickness and surface morphology, respectively.

AS1-3 In-Situ and in-Vacuo Studies on Area Selective Atomic Layer Deposited Ruthenium Films on Silicon and Silicon Oxide*, **Sebastian Killge**, J. Reif,* Technische Universität Dresden, Germany*; M. Knaut, M. Albert,* Technische Universität Dresden, Institute of Semiconductor and Microsystems (IHM); Chair of Nanoelectronics, Germany*; J. Bartha, T. Mikolajick,* Technische Universität Dresden, Germany

We present a thermal activated inherent area selective atomic layer deposition (*thALD*) of ruthenium (*Ru*) on crystalline silicon (*cSi*) wafer and silicon oxide (*SiO_2*)interfaces.

The selective deposition is based upon the inhibited nucleation of ruthenium on oxide surfaces such as SiO_2 compared to Si and metal surfaces. ThALD ruthenium (5-20 nm thick) deposited with the organometallic precursor ECPR [(ethylcyclopenta-dienyl)(pyr-rolyl) ruthen-ium(II)] and molecular oxygen [1, 2] on 4 inch silicon [100] wafers with a pattern of cSi dipped by diluted hydrofluoric acid (*HF*), and native silicon oxide (1.8 nm).

In our experiments, the pattern on the wafer was created by lithography with AZ® 5214 E resist. A dip with 0.5% HF (30 s) was used to remove the native oxide film on cSi and to create a hydrogen-terminated surface. Immediately afterwards, the resist was stripped by a treatment with acetone, 2-propanol, and clean water (conductivity 0.05 µS/cm). After drying, the wafer was transferred into ALD tool for deposition within less than 5 minutes.

As shown in [2-4], the initially incubating and nucleation periods strongly depend on the deposition temperature. On HF-dipped cSi after a nucleation period of 10 ALD cycles a steady-state Ru-on-Ru(Ox) growth with a GPC of ca. 0.9 Å was observed (Fig. 1) at 180 °C. In the linear steady-state region the GPC was nearly independent on the deposition temper-ature [2]. On native SiO_2, only isolated islands of Ru were formed in negligible quantity after 150-180 ALD cycles, consisting of non-stoichiometric Ru / Ru(Ox). Here, growth started after 180 ALD cycles, whereas on HF-dipped Si a 16 nm thick Ru film (Rs= 14,2 Ω/□; ρ= 22,72 µΩ*cm) has been deposited already (Fig. 2). A higher quality of selectivity became be achieved by combining ALD with selective etching using an O_2 or O_3 purge after a certain number of ALD cycles (Fig. 3). As we demonstrated earlier [1, 2], purge steps with molecular hydrogen (*H_2*) during Ru-ALD can prevent blister formation.

AS1-6 Nucleation and Growth in Localized Thermal Atomic Layer Depostion*, **Bart de Braaf**, K. Storm,* Eindhoven University of Technology, Netherlands

We explore the possibility of achieving area selective ALD by modifying the temperature profile on the substrate. The technique keeps the majority of the substrate at a low temperature, suppressing the surface chemical reaction, while a small area is heated to allow the reaction to locally proceed. A practical example of this technique is the ALD process of Si_2H_6(1). Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modeling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized dots and lines given an inhomogeneous temperature profile. We show that the temperature profile can direct substrate deposition and control the connectivity and size of the domain deposited on the substrate.

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Area Selective ALD
Room On Demand - Session AS2
Selective ALD by Area-Deactivation

AS2-1 Gradient Area Selective Deposition using Ti Precursor Inhibitor for Seamless Gap-filling in 3D Nanostructure Pattern*, Chi Thang Nguyen,* Incheon National University, Korea (Republic of)*; E. Cho,* Samsung Electronics, Korea (Republic of)*; J. Park,* Hongik University, Korea (Republic of)*; B. Gu,* Incheon National University, Korea (Republic of)*; B. Shong,* Hongik University, Korea (Republic of)*; H. Lee,* Incheon National University, Korea (Republic of)

Atomic layer deposition (ALD) is a thin film deposition technique with excellent uniformity and conformality at nanoscale due to its unique surface self-saturated reactions of precursors and counter reactants. However, the isotropic growth of ALD is one of the bottlenecks to enable the seamless gap-filling in high aspect ratio structures, such as holes and trenches because the opening of structures is closed off at a certain thickness, resulting in formation of a void. In this work, we introduce an area-selective ALD (AS-ALD) process to realize seamless deposition in 3D nanostructures by using a gradient adsorption of a Ti source precursor inhibitor namely $TiCp^*(OMe)_3$. The $TiCp^*(OMe)_3$ inhibitor can block the growth of TiO2 ALD (using Tetrakis(dimethylamido)titanium-TDMAT precursor) up to 900 cycles (ca. 50 nm) with a high selectivity of ca. 91.3 %. For the gradient AS-ALD, the density of inhibitor adsorption inside 3D structures is controlled by exposure of the $TiCp^*(OMe)_3$ inhibitor, and the deposition of TiO_2 is inhibited in the following TiO_2 ALD depending on the surface concentration of the inhibitor. The results show the ability to control the growth of TiO_2 ALD in the hole pattern (aspect ratio =16). The gap can be filled up from bottom to determined position inside hole without any seams in the centerline. Theoretical calculations by Density functional theory (DFT), Monte Carlo (MC) simulation show high consistency with the experimental results. The concept of gradient AS-ALD could be extended to other ALD materials system for better and simplified process in many various applications.

AS2-4 Selectivity Loss Mechanisms in TiO_2 Area Selective Deposition on Dimethylamino-Trimethylsilane Passivated SiO_2*, Rachel Nye,* North Carolina State University*; K. Van Dongen, J. Clerix,* KU Leuven, Belgium*; G. Parsons,* North Carolina State University*; A. Delabie,* KU Leuven, Belgium

Titanium oxide (TiO_2) area-selective deposition (ASD) has been studied for applications such as hard masks for tone inversion, dielectric layers, solar cells, and photocatalysis due to the etch resistance, high dielectric constant, and high refractive index of TiO_2. While these studies[1] have successfully demonstrated several nanometers of selective deposition using various passivation, activation, and defect mitigation techniques, there is still work needed to understand selectivity loss mechanisms in order to further expand selectivity windows to reach commercial requirements. Herein we evaluate selectivity loss mechanisms of TiO_2 deposited on trimethyl-silane passivated SiO_2 substrates from $TiCl_4/H_2O$.

Dimethylamino-trimethylsilane (DMA-TMS) passivates SiO_2 substrates with a 300 s exposure at 250 °C while Si, TiO_2, TiN, and Ru surfaces remain unaffected.[2] This DMA-TMS passivated SiO_2 limits TiO_2 surface coverage to ~5% after 100 cycles (3.8 nm on the growth surface) at 150 °C, as characterized by scanning electron microscopy (SEM) and Rutherford backscattering spectrometry (RBS) (Fig. 1).

Nuclei on the non-growth surface were analyzed with SEM and atomic force microscopy (AFM) to gain insight on nucleation mechanism, adsorption kinetics, and possible impact of diffusion (Fig. 2). Particle size distributions (PSDs) reveal a high concentration of small nuclei even for high cycle numbers. This indicates new nuclei generation on the non-growth surface during deposition. Kinetic modeling[3] was employed to fit experimental data according to this information using an estimated site generation rate of $4.6x10^{-5}$ sites cm^{-2} $cycle^{-1}$ and a 30-cycle nucleation delay. Modeling results correspond to a thickness of ≈4 nm TiO_2 while maintaining 90% selectivity ($t_S = 0.9 = 4.02$ nm).* Furthermore, we compare PSDs at low (150 °C) and high (300 °C) deposition temperatures to evaluate changes in species diffusivity and loss of effectiveness in the passivation layer. Finally, this insight is applied to develop techniques for extending TiO_2 selectivity windows, including repeated passivations and periodic etching to mitigate defects. The improved understanding on TiO_2 selectivity loss identifies effective strategies to increase selectivity to reach advanced technology nodes.

AS2-7 Area-Selective Atomic Layer Deposition of Al_2O_3 on SiO_2 Vapor-Functionalized with Small-Molecule Aminosilanes*, Wanxing Xu,* Colorado School of Mines, USA*; P. Lemaire, K. Sharma, D. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines, USA

With feature dimensions of state-of-the-art semiconductor devices moving toward the 5 nm node and beyond, device fabrication based on top-down approaches is becoming ever more challenging. Recently, area-selective atomic layer deposition (ALD) has evolved as a promising method to fabricate well-defined patterns from the bottom-up with atomic-scale accuracy. Within the different approaches for area-selective ALD, the preparation of patterned substrates with material-selective organic functionalization offers a promising direction for achieving self-aligned patterns over large areas. In this study, we focus on area-selective ALD of Al_2O_3 on functionalized SiO_2 with small-molecule aminosilanes through the vapor phase. Using *in situ* optical surface diagnostics, we investigate the atomistic-scale mechanism that leads to the reaction of the ALD precursors with the functionalized SiO_2 surface.

To inhibit the ALD of Al_2O_3 on SiO_2, SiO_2 substrates were exposed to bis(dimethylamino)dimethylsilane and (*N*, *N*-dimethylamino)trimethylsilane through the vapor phase. *In situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy shows that the aminosilanes react with almost all of the surface –OH groups, thereby rendering the surface unreactive toward dimethyl aluminum isopropoxide (DMAI), which was used at the aluminum precursor in conjunction with and H_2O. *In situ* ATR-FTIR spectroscopy was also used to monitor the reactions on the SiO_2 surface during Al_2O_3 ALD while film growth was monitored using *in situ* four-wavelength ellipsometry. Our experiments show that growth initiation on the functionalized SiO_2 surface may occur due to DMAI molecules that remain strongly bound to the SiO_2 surface after the purge step, suggesting that the growth on functionalized SiO_2 surface could be further inhibited by lowering the precursor dose (see Figure 1). We further show that the growth inhibition of an additional 20 ALD cycles is obtained on functionalized SiO_2 when the DMAI dose dropped from 3.2 Torr·s to 0.4 Torr·s (see Figure 2). Finally, we show that the less reactive precursor, DMAI, leads to better growth inhibition on functionalized SiO_2 compared to trimethylaluminum.

Area Selective ALD
Room On Demand - Session AS3
Inherently Selective Processes

AS3-1 Impact of Precursor Structure on the Initial Growth Trends of Atomic Layer Deposited Al_2O_3 Films on Chemical Oxide and Hf-last Silicon*, Holger Saare,* *G. Parsons,* North Carolina State University

Aluminum oxide thin films are utilized in numerous applications, such as gate oxides, heat sinks, barrier materials, and more. Atomic layer deposition (ALD) of Al_2O_3 using trimethylaluminum (TMA) as a precursor is one of the most extensively studied ALD processes, owing to its high vapor pressure, high reactivity, and self-terminating reactions. However, for area-selective deposition (ASD) applications, such as next-generation nanopatterning, this reactivity leads to poor selectivity, as TMA rapidly reacts with most surfaces. Thus, alternative precursors for the selective deposition of Al_2O_3, which result in selectivity between different surfaces while maintaining high film quality, need to be considered.

In this work we compare initial growth trends of Al_2O_3 ALD on hydrogen-terminated Si (Si-H) vs hydroxyl-terminated Si (Si-OH) surfaces using three different Al precursors and H_2O as the oxygen source. Triethylaluminum (TEA), dimethylaluminum chloride (DMAC), and TMA are chosen as the Al precursors due to comparable variations between their structures. This enables us to determine the effects that alkyl ligand length and the presence of chloride groups have on the growth selectivity. The growth trends are studied in the temperature range of 150-250 °C and characterized using *in-situ* spectroscopic ellipsometry (SE) and *in-situ* Auger electron spectroscopy (AES).

Measured thickness evolution exhibits similar behavior for all three precursors as shown in Figure 1. On the Si-OH starting surface, the first cycle shows an accelerated growth rate due to higher precursor uptake and then proceeds in a steady-state manner characteristic to ALD. The resulting growth rates are 0.13, 0.11, and 0.10 nm/cycle for TMA, TEA, and DMAC, respectively. Meanwhile, the growth on the Si-H surface exhibits a delay due to the lack of hydroxyl groups. The growth rate accelerates as more nuclei are deposited and eventually reaches steady-state growth rate as the islands coalesce into a uniform film. While TMA results in the highest growth rates, it leads to the lowest selectivity throughout the cycles as shown in Figure 2. The highest selectivity is achieved using TEA, owing to low rate of nucleation on the Si-H surface. Chemical analysis using AES confirms the growth trends present and shows that the steady-state growth rate is decreased due to -CH_3 groups present on the surface.

These results provide vital insight into the importance of precursor selection for area-selective ALD applications and open the pathway to realizing selective Al_2O_3 deposition based on inherent substrate selectivity.

AS3-2 Inherently Area-Selective Atomic Layer Deposition for High-*K* Dielectrics by Catalytic Local Activation*, Jeong-Min Lee,* *H. Kim, J. Ahn, W. Kim,* Hanyang University, Korea

In modern technologies, area-selective atomic layer deposition (AS-ALD) which allows for precise pattern placement with nanoscale dimensions through an additive approach has attracting tremendous interests as a solution to implement the bottom-up nanopatterning for the future semiconductor fabrication. More recently, inherent AS-ALD, which exhibits substrate-dependent deposition selectivity without the use of surface-deactivating molecules, can be expected to offer enormous advantages over conventional inhibitor-assisted AS-ALD in terms of more simplified process and avoiding inhibitor-associated contamination issues. Therefore, we report a methodology for achieving inherently selective deposition of high-k dielectric thin films by catalytic local activation on noble metal substrate. In this work, we demonstrate that AS-ALD of $Hf_{1-x}Zr_xO_2$ films can be achieved by chemo-selective adsorption of precursors which arises from catalytic dissociation of a coreactant molecules on noble metal surfaces like Pt and Ru. For this purpose, O_2 gas was utilized as a mildly oxidizing coreactant and tris(dimethylamido)hafnium/zirconium-cyclopentadienide (CpHfZr) precursors which require strong oxidizing agents were used to deposit selective $Hf_{1-x}Zr_xO_2$ thin films. Finally, we successfully achieved inherent selectivity greater than ~5 nm on both blanket- and Si/Pt-patterned substrates. This approach for achieving inherent selectivity expands the potential utility of bottom-up nanopatterning processes for next-generation nanoelectric applications.

AS3-3 Integration of Two Atomic Layer Depositions in a Sequence for Area Selective Deposition of Two Materials*, Seung Keun Song,* *J. Kim, G. Parsons,* North Carolina State University

The semiconductor industry is now entering the new era of ~3 nm patterning in electronic device manufacturing, leading to many challenges in high volume manufacturing. To achieve satisfactory quality in nanoscale device features, in addition to extreme UV (EUV) lithography, “bottom-up” growth of thin films through area selective deposition (ASD) is becoming a key technique in the manufacturing flow.

ASD deposits a thin film of material on a target region of a substrate while maintaining clean surfaces on adjacent, non-growth regions by translating chemical surface information. ASD methodologies have been demonstrated in roughly two ways, namely 1) locally pre-modifying the substrate to passivate or activate one region or/and 2) integrating etch-back/passivation steps in deposition cycles to suppress unfavorable growth. Many ASDs have focused on selectively depositing one material on one target surface. However, in this talk, we report ASD of two materials (TiO_2 and W) on two different regions (SiO_2 and Si-H) of one substrate by integrating two ASDs into one process sequence.

Previously, our group reported an ALD/ALE process for TiO_2 ASD on SiO_2 vs Si-H. We also reported W ASD on Si-H vs SiO_2 using W ALD (SiH_4/WF_6), which is reverse selectivity compared to the TiO_2 ASD. Herein we examine two scenarios for the integration of two ASD processes (TiO_2 ASD and W ASD) to achieve ASD of two materials without significant interference, which are W 1st (W ASD + TiO_2 ASD) and TiO_2 1st (TiO_2 ASD + W ASD). (Fig. 1) After careful analysis of in situ quartz crystal microbalance (QCM) for two scenarios, TiO_2 1st case is confirmed as a feasible integration sequence for ASD of TiO_2 and W on SiO_2 and Si-H, respectively. After the integrated sequence of TiO_2 ALD/ALE and W ALD, ~5 nm of TiO_2 and ~7 nm of W thin films are confirmed by TEM. Furthermore, we also find that intermediate treatment such as HF dip between ASDs helps W growth on Si-H by regenerating hydrogen terminations.

Beyond the demonstration of selective deposition, these results also explain deposition difference on non-patterned vs patterned substrate after the integrated ALD sequence. We believe these findings give an important insight into integrating two or more selective processes including ALD, ALE, CVD, and CVE for true bottom-up nanofabrication.

AS3-4 Substrate Dependent Absorption of Volatile Antimony Pentachloride during Vapor Phase Poly(3,4-ethlenedioxythiophene) Polymerization*, JUNGSIK KIM,* *G. Parsons,* North Carolina State University

Bottom-up processing has drawn attention in the field of nanoelectronics due to its capability to produce transistors with feature size less than 5 nm. Based on inherent chemical selectivity on different surfaces, area-selective deposition (ASD) is the primary technique to obtain bottom-up 3D patterning. Although many studies regarding ASD of inorganic materials have been addressed, there are few studies on ASD of polymers. Selective polymer deposition could play an important role in nucleation inhibitors/initiators, blocking masks, and air-gap applications. We have previously reported ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) by o-MLD using a volatile liquid $SbCl_5$ oxidant and 3,4-ethylenedioxythiophene monomer (EDOT).[1] During the o-MLD process, PEDOT showed selective growth on thermally grown silicon dioxide (SiO_2) vs hydrogen-terminated silicon (Si-H).

In this work, the mechanism of PEDOT ASD on SiO_2 and Si-H was studied. Compared to SiO_2 substrates, PEDOT showed a nucleation delay on Si-H surfaces. We believe that the growth inhibition on Si-H is due to the $SbCl_5$ reaction with Si-H surfaces. As shown in **Figure 1**, thermodynamic calculation shows that the $SbCl_5$ oxidant is readily reacted with Si, whereas no reaction is observed on SiO_2 surfaces. To clearly understand the $SbCl_5$ dose effects on PEDOT selectivity, different $SbCl_5$ exposure conditions were systematically investigated. Using the oMLD process, we demonstrated ~20 nm of PEDOT ASD on SiO_2/Si-H patterned substrates as shown in **Figure 2**.

These results suggest that minimizing $SbCl_5$ exposure is a key factor into enhancing PEDOT selectivity. In this regard, a fast net growth rate by the CVD process was employed to improve the selectivity. By decreasing the $SbCl_5$ exposure time with the fast growth rate, unfavorable nucleation on Si-H was effectively controlled, leading to better PEDOT ASD compared to MLD. An analytical nucleation model was implemented to quantify ASD between MLD and CVD processes. These studies give an important insight into developing conjugated polymer ASD and play a pivotal role in improving the ASDs.

AS3-7 Inherent Selective CVD of Amorphous HfO_2/TiO_2 Nanolaminate for Nanoscale Patterning*, Yunil Cho,* *J. Huang,* University of California at San Diego*; C. Ahles,* University of California San Diego*; K. Wong, S. Nemani, E. Yeah,* Applied Materials*; A. Kummel,* University of California at San Diego

Nanoscale patterning is one of the key interests in the semiconductor industry. For nanoscale patterning applications, inherently selective deposition methods (no passivants) are being studied to use in conjunction with double patterning techniques as shown in Fig. 1. This chemically based patterning is needed in backend fabrication when multiple metals and low k dielectric layers such as SiCOH (hydrophobic porous carbonized silica) are employed. For selective deposition in backend fabrication, water-free deposition is desirable since it induces higher selectivity [1] and prevents damage of metals and SiCOH.

Previously, the inherent selective CVD of TiO_2 was studied on Si, SiO_2 and SiCOH. Around 17 nm and 40 nm of TiO_2were deposited on Si and SiO_2, respectively, with less than 0.1 nm on SiCOH. However, due to nano-crystallization, the films had rough surfaces (Fig. 2.) which has to be reduced for nanoscale patterning applications. By forming nanolaminate structures of two different oxides, this crystallization can be surpressed[2,3]. In the present study, sequential pulsed CVD at 300˚C sample temperature using titanium isopropoxide and hafnium tert-butoxide to form an amorphous HfO_2/TiO_2 nanolaminate film was studied.

Due to inherent (passivation-free) surface reactivity difference of each precursor, HfO_2/TiO_2 nanolaminate films were selectively deposited on Si and SiO_2 in preference to SiCOH. By controlling HfO_2 and TiO_2 sublayer thickness and the Hf:Ti ratio, amorphous and selective deposition of the HfO_2/TiO_2 nanolaminate film could be achieved simultaneously. Thick films were selective deposited: ~20 nm of amorphous HfO_2/TiO_2 nanolaminate was selectively deposited on Si and SiO_2 in preference to SiCOH (<0.1 nm) with an RMS roughness <1 nm as shown in Fig. 3.

To check for nanoscale patterning application, selective deposition of the HfO_2/TiO_2 nanolaminate film was tested on a Cu/SiCOH nm scale patterned sample. TEM imaging (Fig. 4) demonstrates that the HfO_2/TiO_2 nanolaminate film can be selectively deposited only on Cu surface even for nanometer scale features.

This study demonstrated high selective oxide deposition by inherent reactivity difference of precursor mediated chemisorption on the nm scale. For nanolaminate structures with 1-2 nm sublayer thickness, crystallization can be suppressed which make this process suitable for patterning.

AS3-10 Optimization of Substrate-Selective Atomic Layer Deposition of Zirconia on Different Forms of Copper Using Ethanol as Precursor Reactant and Surface Pre-Treatment*, Soumya Saha,* University of Illinois at Chicago*; N. Anderson,* Intel Corporation*; G. Jursich, C. Takoudis,* University of Illinois at Chicago

Copper is currently the material of choice for making interconnects in semiconductor devices and zirconia, having a high dielectric constant, could replace silicon dioxide as the gate dielectric material in the near future. Atomic layer deposition (ALD) has emerged as the 'bottom-up' technique due to its capability of depositing uniform ultra-thin films and potential for area selectivity. In this study, zirconium dioxide was selectively deposited on silicon and not on copper for at least up to 100 ALD cycles using tris(dimethylamino)cyclopentadienyl zirconium as the zirconium precursor and ethanol as the precursor reactant in a custom made ALD system (Patent #10214817). Typically, copper is electroplated and then chemical mechanical polished. Here, both electroplated (EP) and electroplated copper with chemical mechanical polishing (CMP) were used for this study and subtle difference in surface oxides on EP and CMP copper and the choice of reactant influenced selectivity of deposition. Under suitable ALD processing deposition was inherently selective on EP copper and could be achieved on CMP copper only after optimizing the deposition process parameters. ZrO_2, selectively deposited via ALD, was characterized using spectral ellipsometry, X-ray photoelectron spectroscopy and extended X-ray absorption fine structure spectroscopy.

Area Selective ALD
Room On Demand - Session AS4
Area Selective ALD Poster Session

AS4-1 Effect of Surface Cleaning Efficacy on Vapor-Phase Cleaning of Cu and Co Using Anhydrous N_2H_4*, Su Min Hwang,* *J. Kim, D. Le, R. Gummadavelly, Y. Jung, J. Veyan,* University of Texas at Dallas, USA*; D. Alvarez, J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas, USA

As the critical dimension of current Copper (Cu) metal line shrinks below 5 nm, the resistivity of Cu is expected to increase drastically, due to electron scattering at the sidewall and grain boundaries.[1] In addition, the high-resistivity liner and diffusion barrier, currently required in the copper interconnects, attribute to the decrease of effective width of Cu. To circumvent this issue, the study of alternative materials to Cu have been reported. Among the various metals, Cobalt (Co) has been proposed as a potential material with comparable resistivity below 7 nm thickness.[2] Several processes on ALD of Co have been reported requiring an additional reduction step to obtain metallic Co. Therefore, it is imperative to explore reducing agents capable of reducing the oxide on Co at low temperatures. Recently, hydrazine (N_2H_4) has been reported as the reducing agent of the Cu oxide due to its higher reduction capability.[3] Inspired by hydrazine's unique characteristics, we explore the feasibility of vapor-phase reduction of Co oxide using N_2H_4 to achieve an ideal metallic Co film in an ALD environment. Additionally, a detailed reduction mechanism of the Co oxide by comparing with Cu oxide will be studied using *in-situ* surface analysis. In this study, we have demonstrated the effect of vapor-phase cleaning on Cu and Co using anhydrous N_2H_4 with its high reduction capability to remove surface contaminants and metal oxide. The Cu film with 1.5 µm thickness and the Co film with 200 nm thickness were deposited on a silicon substrate using electroplating and sputtering, respectively. The preparedCu and Co films were treated with ALD-like multiple exposures of N_2H_4 in the temperature range of 100 – 400 °C. Each cycle consisted of 0.5 s N_2H_4 exposure and 120 s Ar purge. The XPS analysis of the Cu samples treated at 200 °C show a significant amount of copper oxide was reduced to metallic copper with an approximate thickness of 1 nm. Meanwhile, the Co samples show the cleaning efficacy at above 350 °C due to the relative stability of the cobalt oxide. In addition, *in-situ* reflection absorption infrared spectroscopy (RAIRS) was employed to elucidate the individual surface chemistry of Cu and Co films during the N_2H_4 exposure step. The detailed experimental results will be presented.

We thank Rasirc Inc. for funding this project and providing the Brute N_2H_4.

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Emerging Materials
Room On Demand - Session EM1
Molecular Layer Deposition

EM1-1 Gas Phase Phosphane-ene Polymer Film Depositions*, Peter Gordon,* Carleton University, Canada*; P. Ragogna,* University of Western Ontario, Canada*; C. McGuiness,* Solvay*; S. Barry,* Carleton University, Canada

Phosphane-ene polymers are a new class of soft material with a wide variety of characteristics. They exhibit orthogonal reactivity for functionalization, polyelectrolyte behavior, and oxygen and metal scavenging[1-3]. These versatile polymers are highly tunable and structurally diverse, depending on the choice of phosphine and cross-linker[4,5].

Previously reported solution-phase synthesis of phosphane-ene polymers[6] have been adapted to a molecular layer deposition (MLD) process. The solution-phase synthetic method employs a photo-initiated radical-assisted polymerization, and we have adapted an A-B-C MLD pulse sequence that includes a plasma step to produce gas-phase radicals. These radicals serve as surrogates for the photo-initiator in the solution-phase method, generating surface-bound radical sites that promote reactivity to generate the polymer. This hypothesis is supported by an absence of film growth if the plasma pulses are omitted.

Thin polymer films were deposited on silicon substrates at 40°C. An optimized pulse sequence of 0.1 s pulse isobutyl phosphine with a 149 s chamber residence time, 60 s argon plasma, 1.0 s tetramethyltetravinylcyclotetrasiloxane with a 149 s residence time, and a 10 s nitrogen purge was used. At a plasma power of 600 W, uniform phosphorus-containing films with a growth per cycle of 0.8 Å and an RMS roughness of 8 nm were produced. Composition has been characterized by XPS, TOF-SIMS, Auger sputtering, and PM-IRRAS.Roughness and growth per cycle were measured with AFM. These properties can be tuned by varying plasma power, yielding a reliable method for fabricating thin phosphane-ene films from gas phase reagents in a stepwise fashion.

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EM1-2 Atomic/Molecular Layer Deposition of Ordered 1D Coordination Polymer Thin Films With Adjustable Electric Conductivity*, Mikko Nisula,* Ghent University, Belgium*; A. Karttunen,* Aalto University, Finland*; E. Solano,* ALBA Synchrotron Light Source, Spain*; P. Kaur, A. Devi,* Ruhr University Bochum, Germany*; G. Tewari, M. Karppinen,* Aalto University, Finland*; M. Minjauw, H. Jena, P. Van Der Voort, C. Detavernier,* Ghent University, Belgium

The prospect of introducing tuneable electric conductivity in hybrid metal-organic coordination polymers could be of high interest for future nanoelectronic applications. As the electronic properties of these materials are strongly dependent on their microstructure, robust synthetic routes for thin films with high degree of ordering and well-controlled thickness are needed not only for practical applications but also for fundamental understanding of transport phenomena in conductive coordination polymers.

In this respect, atomic/molecular layer deposition (ALD/MLD) is uniquely suited for the fabrication for high-quality coordination polymers thin films. While the technique is already established for passive coatings such as barrier layers, intrinsically conductive materials could be achieved by broadening the range of available ALD/MLD processes to redox non-innocent molecules.

With this goal in mind, we investigate the deposition of hybrid thin films based on several dithiooxamides (DTOA) with Cu as the metal site. The good overlap between the Cu d-orbitals and the frontier orbitals of the sulphur-containing ligand should be beneficial towards charge delocalization and electric conductivity. The redox-active DTOA ligands open up the possibility of further tuning the thin film properties by adjusting their oxidation state.

High out-of-plane ordering is observed in the resultant thin films suggesting the formation of a well-ordered secondary structure by the parallel alignment of the 1D polymer chains. As postulated, we show that the electrical conductivity of the thin films is highly dependent on their oxidation state. The as-deposited films are nearly insulating with electrical conductivity below 10^{-10} S/cm with semiconductor-like temperature dependency. By taking advantage of the catalytic properties of the open Cu nodes, we utilize H_2 at elevated temperature to partially reduce the thin films. With N,N'-dimethyldithiooxamideas the ligand, the reduction leads to an increase in the electrical conductivity by 8 orders of magnitude. In this high-conductance state, the thin films exhibit metallic temperature dependency of conductivity. On the other hand, with diethyl- and dipropyl variants, the conductance remains unchanged. With the help of DFT modeling, we link the observed conductance increase to combined structural change and charge carrier injection. Namely, we observe the formation of a half-filled conduction band that arises from the formation of extended $(\text{-Cu-S-})_n$ conduction pathways between neighbouring polymer chains.

**EM1-3 Oxidative Molecular Layer Deposition of Conjugated Amine Polymer Thin-Films*, Quinton Wyatt*, *M. Vaninger, T. Heitmann, H. Kaiser, M. Young,* University of Missouri, Columbia

Electrically-conductive and redox-active polymers such as polyethylenedioxythiophene (PEDOT), polypyrrole (PPy), and polyaniline (PANI) have applications in flexible electronics, energy storage, electrochemical desalination, and chemical sensors. In each of these applications, delivering conformal, thin-film polymer coatings is attractive to provide lower weight, faster charging, and higher sensitivity. Unfortunately, traditional approaches for polymer synthesis struggle to deliver uniform thin film coatings onto 3D substrates. In general, molecular layer deposition (MLD) is an attractive route for the formation of these polymer coatings because MLD growth involves alternating self-limiting surface reactions and inherently provides uniform coatings on 3D substrates. Previous work reported a scheme for MLD of conductive and redox-active polymers employing sequential doses of monomers and a chemical oxidant ($MoCl_{5}$-), termed *oxidative* MLD or "oMLD," and demonstrated the formation of PEDOT films using this approach. In this report, we expand on this prior work and study oMLD of amine-containing conductive and redox-active polymers including PPy, PANI, and their derivatives using alternating exposures of monomers and $MoCl_5$ oxidant. We perform both in-situ and ex-situ experimental measurements to study the growth behavior of these polymers, and identify unexpected monomer-dependent growth. We also measure the conformality and the electrical and electrochemical properties of the resulting films. We find that pyrrole and substituted-aniline both undergo self-limiting surface reactions to form conformal, electrically-conductive and redox-active polymer films. We also identify that copolymer alloys of PPy and substituted-PANI growth chemistries yield improved electrochemical properties over isolated monomer chemistries. Our results provide new insights into the oMLD growth mechanism in general, and offer the prospect for molecular-level control of conjugated polymer structures delivered in a conformal, thin-film geometry.

EM1-6 Converting Molecular Layer Deposited Alucone Films into Al_2O_3/alucone Hybrid Multilayers by Plasma Densification*, Juan Santo Domingo Peñaranda,* Ghent University, Spain*; M. Nisula,* Ghent University, Finland*; S. Vandenbroucke, M. Minjauw,* Ghent University, Belgium*; J. Li,* Ghent University, China*; A. Werbrouck, J. Keukelier,* Ghent University, Belgium*; A. Pitillas Martínez,* IMEC, Spain*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Alucones are one of the best-known films in the Molecular Layer Deposition (MLD) field, mainly due to their flexibility, but their stability in air is a concern. On the other hand, Al_2O_3 offers very low water vapour transmission rates (WVTRs), at the expense of strain sensitivity even for thin layers. As a consequence, alucone/Al_2O_3 nanolaminates withhold potential for synergistic behaviour. The impermeability of Al_2O_3 will impede moisture from entering the stack and, when it enters, it will encounter an alucone structure where it will absorb. Therefore, these nanolaminates can create a very tortuous path for water molecules and may lower the effective diffusion constant to the substrate.

In this work, we prove that alucone/ Al_2O_3 nanolaminate synthesis can be successfully performed by alternating alucone MLD growth with static O_2 plasma exposures. Upon plasma treatment, only the top part of the alucone is densified into Al_2O_3, while the rest of the film remains relatively unaltered. X-ray reflectivity (XRR) and x-ray photoelectron spectroscopy (XPS) depth profiling show that the process yields a bilayer structure, which remains stable in air. Fourier-transform infrared spectroscopy (FTIR) measurements show that Al_2O_3 features are generated after plasma treatment, while the original alucone features remain, confirming that plasma treatment results in a bilayer structure. Also, an intermediate carboxylate is created near the interface. Calculations of Al atom density during plasma exposure point towards a partial loss of Al atoms during plasma treatment, in addition to the removal of the glycerol backbone.

The effect of different process parameters has been studied. Densification at the highest temperature possible (200ºC) has the best alucone preservation without hindering its thermal stability. In addition, operating at the lowest plasma power is found the most beneficial for the film, but there is a threshold that must be surpassed to achieve successful densification. About 70% of the original alucone film thickness can be expected to remain after densification, but thicker films may result in more diffuse interfaces. Additionally, this process has also been successfully performed in multilayers, showing potential for encapsulation applications.

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Emerging Materials
Room On Demand - Session EM11
Emerging Materials Poster Session

EM11-1 Strategies for High-Quality Nitride and Oxide Stacks by Plasma ALD*, Yi Shu,* Oxford Instruments Plasma Technology, UK*; F. McGuire,* Oxford Instruments Plasma Technology*; A. Kurek, O. Thomas,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands

Many applications in industry require the deposition of nitrides and oxides with high purity and with high-quality interfaces. The focus of most atomic layer deposition (ALD) studies is on the deposition of a single layer in a dedicated deposition chamber. This contribution highlights a set of strategies for high-quality nitride and oxide stacks deposited by ALD in a single run in a single chamber. As an example, an HfO_2/SiN_x multilayer is demonstrated with <5% oxygen in the nitride.

Low oxygen content is a challenge for nitride deposition, especially when lines and chambers might contain oxygen and water traces from a previous deposition. To demonstrate a high-quality oxide and nitride stack, HfO_2 using TDMAHf and O_2 plasma and SiN_x using BTBAS and N_2 plasma are employed. The depositions are carried out in a FlexAL system in a single run and to get the best SiN_x the residence time was minimized by a combination of turbo pumping, chamber heating and pressure and flow control.[1] For other ALD nitride processes substrate biasing could be employed to lower oxygen content, but in the case of SiN_x this is less effective.[2] When switching from oxide to nitride deposition, the following strategies are employed:

- Strong purging and pumping of any gas lines that could contain oxygen or oxygen byproducts.
- TDMAHf precursor pulses to scavenge possible oxygen by-products.
- Plasma treatment of the chamber and wafer surface.

After the subsequent deposition of the nitride the surface is exposed to a plasma post-treatment to further densify the material and protect it against oxidation. Using this strategy an alternating stack of HfO_2 and SiN_x was deposited with individual layer thicknesses of 20 nm. XPS depth analysis indicated that even with this relatively fast switching, oxygen content levels <5% were obtained for SiN_x (XPS analysis by Dr. Shihong Xu, nanoFAB Centre, University of Alberta). This example and general strategies for such oxide and nitride stacks will be presented.

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EM11-2 Compositionally Graded Laminate ALD Films*, Alexandru Pavel, V. Vorsa,* Greene Tweed, Inc.

To prevent contamination of microelectronic devices during semiconductor processing, chamber components of semiconductor tools are often coated with high purity ceramic coatings such as alumina or yttria that exhibit high resistance to plasma erosion in halogen environments.However, even these materials exhibit erosion over time leading to lower yield and costly down time, especially as the industry moves to smaller node sizes.

To overcome these limitations, there has recently been a major effort to find new coating materials and processes leading to improved plasma erosion resistance. There are now emerging plasma-resistant coatings deposited by atomic layer deposition (ALD). Advantages of ALD include conformal, dense, and pinhole-free film that can coat complex 3D shapes and high-aspect ratio holes.

One weakness with many coatings, including ALD, is the transition from one material composition to another.For example, the transition from substrate to film or from one film composition to another.Typically, in ALD, the film-substrate interface transitions abruptly within an atomic spacing of 1-2 Å.This can lead to high stress gradients confined to a narrow planar region potentially leading to poor film adhesion, especially where smooth surfaces and large CTE mismatches are present.

To overcome this drawback, ALD films can be deposited in such a way (US20200131632A1) that the composition is smoothly transitioned from one material to another, thus avoiding narrowly confined stress gradients.In this work, we present plasma resistant multi-layer coatings that exhibit excellent bonding of films to substrates formed by gradually varying the chemical composition from substrate to film and from one film type to another in a technique called Compositionally Graded Laminates (CGL).Examples of Compositionally Graded Laminate films of Y2O3-Al2O3, Y2O3-SiO2, and Y2O3-ZrO2 systems will be presented.

In addition to the semiconductor industry, this technique may be used to prepare and/or to coat substrates that form components useful in a variety of industries, especially those where components may be exposed to high temperatures and/or corrosive chemicals. For example, Compositionally Graded Laminates may be used on components that are found in equipment or devices used in aerospace, energy storage, pharmaceutical production, food processing, oil field applications, military and/or maritime applications, industrial manufacturing, and scientific and/or diagnostic instrumentation.

EM11-3 *In Situ* Electrical Conductance to Measure Vapor Phase Infiltration (VPI) Doping Kinetics of Semiconducting Polymers*, **Kristina Malinowski**, S. Gregory, O. Hvidsten, A. Jungreis, M. Losego,* Georgia Institute of Technology

This poster will show our development of *in situ* electrical conductance measurements during vapor phase infiltration (VPI) of polyaniline (PAni) thin films with titanium tetrachloride ($TiCl_4$) to achieve electrical doping. *In situ* measurements during vapor phase processes provide abundant information about reaction kinetics and mechanisms that could not be acquired with *ex situ* data alone. The field of vapor doping semiconducting polymers lacks a robust understanding of doping mechanisms and their respective kinetics. Therefore, the vapor doping community stands to benefit from the implementation of *in situ* measurements. Here, we demonstrate how *in situ* conductance correlates with *ex situ* characterization and propose a sequence of *in situ* doping mechanisms. Dosing and holding $TiCl_4$ in a chamber where hydroxyl groups are present can lead to both oxidative and acid doping of PAni films. The$TiCl_4$ vapor can directly oxidatively dope PAni while the HCl byproduct of $TiCl_4$+ -OH can lead to acid doping. During the first dose and hold of $TiCl_4$, *in situ* conductance measurements show that varying the $TiCl_4$ dose pressure changes the rate and total conductance. Then, purge, pump and isolate steps remove unentrapped $TiCl_4$ from the chamber. Dosing and holding H_2O allows further acid doping, oxidative dedoping and oxide formation. Acid doping is in competition with dedoping and oxide formation to increase and decrease conductance, respectively. The *in situ* conductance measurements show decreasing conductance rates with increasing initial $TiCl_4$ pressures, suggesting that acid doping dominates at low pressures and dedoping and oxide formation dominates at high pressures. The *ex situ* characterization of the thin films validates these suggested mechanisms. Opposite pressure-conductance correlations between the $TiCl_4$ dose and H_2O dose present an opportunity for optimizing PAni conductivity, aided by a thorough understanding of *in situ* kinetics. PAni doping can be further controlled by managing the reactor wall chemistry. If the reactor is first exposed to a precursor reactive towards hydroxyls but does not create an acid byproduct (for example trimethyl aluminum, TMA), then the walls can be passivated. Consequently, when $TiCl_4$ is dosed, it does not react with the passivated walls, and HCl is not formed, so only oxidative doping occurs. During the subsequent water dose, the potential for acid doping is reintroduced through HCl formation within the film. *In situ* measurements demonstrate that this effectively isolates the two doping mechanisms. Thus, *in situ* measurements show promise in aiding design of complex processes for vapor doping of conductive polymers.

EM11-4 Atomic Layer Deposition of Yttrium Oxide using a Liquid Yttrium Precursor, Y-08*, M. Kim,* EMD Performance Materials, Korea (Republic of)*; S. Lee,* EMD Electronics, Korea (Republic of)*; M. Fang, J. Aldo, J. Woodruff, R. Kanjolia,* EMD Performance Materials*; **Bhushan Zope**,* EMD Electronics, USA*; S. Ivanov,* EMD Performance Materials

Yttrium Oxide (Y_2O_3) films deposited by ALD have been extensively studied as a promising high-k material for future device manufacturing such as in MOSFETs or memory applications due to its wide band gap (~5.5 eV), high permittivity (>10), and high thermal stability. Pure or doped Y_2O_3 containing films have also been used in other applications such as in solid oxide fuel cells, protective coatings, photonics, and quantum information processing.

Herein, we report the studies of atomic layer deposition (ALD) of Y_2O_3 thin films using a newly developed volatile, scalable, liquid yttrium precursor, Y-08, with ozone and/or water as co-reactants.

A comparison of oxygen sources shows that "ozone followed by water" leads to a higher growth per cycle {0.81 Å/cycle} compared to either ozone-alone {0.51 Å/cycle}, or water-alone {0.16 Å/cycle}. The ALD window starts at 310 °C on the system tested, and the growth/cycle is 1.09 Å/cycle when saturation is achieved with both the Y-08 and oxygen sources doses.The refractive index ranges from 1.90 to 1.95. XPS analysis confirms that the bulk of film consists of exclusively oxygen and yttrium; but there was some carbon contamination on the film surface.

An yttrium oxide film deposited on a via with 20:1 aspect ratio (1800-nm deep, and 90-nm wide) shows excellent conformality when characterized by SEM (Figure 1), with film thickness ranging between 22.5 and 26 nm outside the via (Figure 2a), and 23 and 26 nm at the via bottom (Figure 2b).

We demonstrate that the liquid nature and high volatility of our new yttrium precursor promotes easier precursor delivery and more controllable ALD processes for manufacturing good quality Y_2O_3 thin films for future semiconductor applications.

EM11-7 Direct sALD of MOF: An Improvement in the Nucleation Behavior*, **Maissa Barr**, S. Nadiri,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; D. Chen, P. Weidler,* Karlsruhe Institute of Technology (KIT), Germany*; S. Bochmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; H. Baumgart,* department of Electrical and computer Engineering, Germany*; j. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; E. Redel,* Karlsruhe Institute of Technology (KIT), Germany

Metal organic frameworks (MOFs), can be described as crystalline three-dimensional porous solids, with a high surface area, which have attracted considerable attention in a wide range of applications e.g. in catalysis,hydrogen storage,gas-separations , thermoelectric applications or as chemical sensors.Up to the present time, low-temperature methods had to be used to grow MOFs thin films today by conventional solution-based techniques. However, traditional growing methods from solution like spin-coating, spray-coating or dip-coating generates MOFs thin films with a rather low film quality and an alarming lack of a precise film thickness control under 1 nm, which renders them unsuitable for most industrial applications and severely limits their future application potential.

Atomic layer deposition (ALD) provides this capability, but is limited by the necessity to use gaseous precursors in vacuum conditions at temperatures above 100°C. However hybrid organo-metalic compunds such as the MOFs are not accessible by ALD due sensitivity to temperature.

In this perspective, we have transferred the principles of ALD to precursors dissolved in liquid solvents. The 'solution ALD' (sALD) method can be implemented in a variety of microfluidic or slot-die processing devices. We have demonstrated that the principles of classical, gas-based ALD —self-limiting surface reactions— are reproduced in sALD. sALD shares the fundamental properties of standard 'gas ALD' (gALD), in particular the self-limiting surface chemistry and the ability to coat deep pores in a conformal manner Furthermore, sALD allows the experimentalist to design new, advantageous, reactions of known semiconductors (oxides, heavier chalcogenides), or to deposit materials otherwise inaccessible to ALD altogether, such as polymers, ionic solids, and metal-organic frameworks. They may be obtained in highly pure, crystalline form at room temperature, either as planar films or as conformal coatings of porous substrates. Based on these advances, we have been able to make the first sALD-derived MOFs.

EM11-10 Thermal ALD Growth of Ir and IrOx Films Using (MeCp)Ir(COD) and Oxygen*, Guo Liu, J. Woodruff,* EMD Electronics, USA*; T. Okamura ,* Merck Performance Materials Ltd, Japan*; D. Moser , R. Kanjolia, B. Zope,* EMD Electronics, USA

Iridium is a noble metal with low oxygen permeability, high chemical stability and high work function. It is one of the most corrosion resistant metals and has a lower bulk resistivity (~5.0 µΩ-cm) than Ru (6.8 µΩ-cm). Due to these unique properties, iridium has been investigated for potential applications in semiconductor devices as gate electrodes, a seed layer or Cu diffusion barrier. On the other hand, IrO_2 can be converted into Ir metal by H_2 reduction, and IrO_2 nanoparticles are some of the best catalysts with potential applications for oxygen evolution in electrolyzers, metal-air batteries, and photoelectrochemical water splitting.

Various Ir precursors have been reported for ALD and CVD growth of Ir and IrO_2 films (1,2). O_2 is the most common oxidizer. Among the known ALD Ir precursors, the cyclodienyl-based (RCp)Ir(COD) (R=Me, Et) have very high thermal stability, and the liquid (EtCp)Ir(COD) precursor has been studied extensively (3,4), while the low melting-point (~40°C) MeCp analogue, (MeCp)Ir(COD), has not received much attention although it is easier to synthesize and has a higher thermal stability than (EtCp)Ir(COD). We have studied the ALD growth behavior of Ir and IrO_2 films using (MeCp)Ir(COD) and O_2 on a number of oxide and metal nitride surfaces in a wide temperature range up to 425°C. High purity Ir films with low O and C have been obtained on oxide and nitride substrates with resistivity down to ~16 µΩ-cm under various deposition conditions as shown in Fig. 1. The growth behavior on oxide surfaces is more complex. IrOx formed under certain conditions with notably higher resistivities. For examples, IrO_x formed at ~ 350°C with O_2 on Al_2O_3 as shown in Fig. 1.

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Emerging Materials
Room On Demand - Session EM2
Organic-Inorganic Hybrid Materials

EM2-1 Toward Industrially Viable ALD/MLD Nanolaminate Films for Flexible Electronics*, Jesse Kalliomaki, T. McKee,* Picosun Oy, Finland

Foldable phones are now a commercially available product, with some manufacturers already several generations into the product cycle. Use of thin film encapsulation solutions (TFEs) in organic electronic manufacturing (OEM) has become more common as they are lighter and enable folding and stretching of a device, unlike conventional encapsulation methods. The commercial demand has created a large driving force to develop the quality, reliability, and process flow integration of TFEs to enable future product iterations. Inorganic films, such as those generally associated with atomic layer deposition (ALD) are vital building blocks for electronic devices due to the variety of properties they offer to a fabrication scheme. One of the main reliability issues TFEs face is that inorganic films are susceptible to crack under mechanical stress, compromising the barrier performance and cutting the lifetime of the device short. [1]

One approach to address this issue is the nanolamination of dense inorganic layers deposited with ALD for enhanced barrier performance, with organic or hybrid molecular layer deposition (MLD) layers to offer enhanced flexibility [2, 3]. To be an industrially viable solution both components of this process need to be scalable to large substrate sizes, have reasonable deposition time and show good stability in ambient conditions. The more studied MLD processes have been shown to be prone to degradation in ambient atmosphere and quickly lose their beneficial properties [4].

We present process development results from a MLD hybrid with several different inorganic linkers deposited in Picosun R-200 advanced ALD reactor on 200 mm Si substrates. The hybrid films analysed with spectroscopic ellipsometer and Drop Shape Analyzer show excellent large area uniformity at OEM friendly temperature of 90 °C. Long term stability was studied with XPS and FTIR in addition to the previously mentioned methods and demonstrates excellent film stability after months of ambient ageing.

Industrially viable MLD processes can be a valuable tool to have in the fields of OEM and flexible electronics. In this work we show that industrial-scale ALD reactors are capable of producing MLD and ALD layers in the same chamber with low thermal budget and that ALD/MLD nanolaminates (Fig 1) can be easily deposited in a single process step on a large-scale substrate, a process that has a potential as a TFE solution.

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EM2-2 Antibacterial Alumochitin Thin Films Grown by Molecular Layer Deposition*, Karina Ashurbekova,* CIC nanoGUNE BRTA , Spain*; K. Ashurbekova ,* Dagestan State University, Russian Federation*; A. Muriqi ,* Tyndall National Institute, University College Cork, Ireland*; L. Barandiaran Larrea ,* CIC nanoGUNE BRTA, Spain*; B. Alonso Lerma ,* CIC nanoGUNE BRTA , Spain*; I. Saric,* University of Rijeka , Croatia*; E. Modin,* CIC nanoGUNE BRTA, Spain*; R. Perez-Jimenez ,* CIC nanoGUNE BRTA, IKERBASQUE, Spain*; . Petravic,* University of Rijeka, Croatia*; M. Nolan ,* Tyndall National Institute, University College Cork, Ireland*; M. Knez,* CIC nanoGUNE BRTA, IKERBASQUE, Spain

Natural chitin and chitinoid materials have outstanding physical and biological properties, which inspired us to develop a process for biomimetic chitinoid organic and hybrid organic-inorganic thin film growth by Molecular Layer Deposition (MLD).

Here, we present a new class of organic–inorganic hybrid polymers called "metallosaccharides", based on sugar-type precursors. For a controlled MLD growth, the hexosamine monosaccharide N-Acetyl-D-mannosamine (ManNAc) was coupled with trimethylaluminum (TMA) repetitively in a cyclic manner for the growth of the hybrid organic-inorganic alumochitin thin films.

The self-limiting behavior of the surface reactions and the growth rate were determined by in-situ quartz crystal microbalance (QCM) and X-ray reflectivity (XRR) studies. The QCM measurements revealed a linear mass increase with the number of MLD cycles. The chemical structures of the coatings were studied with ex-situ X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Characterization of the film structure, morphology, and conformality were performed by High-resolution transmission electron microscopy (HR-TEM), showing uniform and conformal alumochitin films wrapping ZrO2 nanoparticles (NPs).

The chemical interaction between ManNAc and TMA, and the possibility of hybrid alumochitin film formation were modeled by density functional theory (DFT). The computed interaction energies between TMA and ManNAc are negative, meaning that there’s a strong interaction between these precursors. Theoretical modeling revealed that the proposed reaction mechanism for the ManNAc/TMA MLD process is energetically favorable.

The evaluation of the antimicrobial activity of the alumochitin thin film against Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacteria was assessed. Bacteria attachment and proliferation on glass substrates, covered with MLD film, were analyzed by confocal microscopy. (Fig. 1S in the ESI) Both types of bacteria grow and proliferate on positive control samples, while neither Staphylococcus aureus nor E. coli bacteria attached to the surface of the alumochitin film. These results show a great antimicrobial activity of alumochitin against gram-positive and gram-negative bacteria, as well as its enormous application potential as bioactive surfaces.

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EM2-3 Mechanics of Flexible ε-Fe_2O_3/Organic Superlattice Thin-Film Magnets

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The little-known iron(III)oxide polymorph ε-Fe_2O_3 has risen intrigue for its ferrimagnetic character and high coercive field, that make it an interesting material for magnetic storage applications.[1] To enhance the appeal of ε-Fe_2O_3 thin-film magnets for flexible electronics, tailoring its mechanically rigid character is however desired. Here we demonstrate tailoring of the mechanical properties of ε-Fe_2O_3 thin films through insertion of Fe-terephtalate interlayers by using the combined atomic/molecular layer (ALD/MLD) deposition technique.[2,3]

We deposited ε-Fe_2O_3 oxide films, Fe-terephtalate (Fe-TP) hybrid films and ε-Fe_2O_3/Fe-TP superlattice thin films using $FeCl_3$ as the Fe metal precursor, H_2O as the oxygen source, and terephtalatic acid as the organic precursor.[2,3,4]Nanoindentation experiments indicate that the insertion of the Fe-TP interlayers in the ε-Fe_2O_3 matrix enables a factor-of-two decrease in elastic modulus for the superlattice films down to 70±20 GPa. In-situ tensile fragmentation testing indicates that the crack onset strain and critical bending radius can be tuned by a factor of three.Modeling of the tensile fragmentation patterns through Weibull statistics shows that cohesive and interfacial shear strain, following the trend for crack onset strain, increase with increasing organic content, while gains for the respective strengths are limited by the simultaneous reduction in elastic modulus. Importantly, we demonstrate through magnetization vs. magnetic field (M-H) measurements that the unique magnetic characteristics of ε-Fe_2O_3 are not sacrificed in the superlattices with enhanced mechanical flexibility. Magnetic characterization of strained films indicates absence of catastrophic failure upon fragmentation and modest debonding of the films, while the improved mechanical characteristics for the superlattices translate to improved preservation of the magnetic characteristics.

The present results are interesting for magnetic storage applications in flexible electronics and highlight the potential of the combinatorial ALD/MLD technique for enhancing mechanical properties of—not only inorganic-organic alloys as known from the past[5]—but also of multilayer structures with inorganic layers thick enough to generate usable functionalities.

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EM2-4 Effect of Vapor-Phase Metal Infiltration on Lithography of PMMA Resist for EUV Applications

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Due to the limitation of resolution with scaling down of feature size, extreme ultraviolet (EUV) was has drawn great attention as the light source for the next-generation lithography process. Unlike the photoresists for UV irradiation, EUV photoresist interacts with secondary electrons. However, the current polymer-based resist has confronted a number of challenges, such as pattern collapsing due to resist thickness, poor EUV adsorption, and etch-selectivity, etc. To circumvent the limitation, research on new materials, particularly metal incorporation with organic resists have been recently reported. With introduction of metal, the hybrid resist can increase the EUV absorption as well as the mechanical stability during the pattern transferring.[2,3] Among the various synthesis of inorganic-organic hybrid EUV resists, vapor-phase infiltration of metal source into existing organic resist using ALD process can be employed. This *ex-situ* process can avoid the complex chemistry and employ the standard fabrication process.

In this work, we have demonstrated the infiltration of Hf into PMMA e-beam resist using ALD process. The PMMA resist is coated on the Si substrate using a spin-coating technique, followed by exposure of TDMA-HF precursor in the ALD chamber at 85 °C. In XPS gas cluster ion beam depth profile, Hf concentration showed 5 to 10 at. % in PMMA film, implying that Hf is distributed in the PMMA resist. Specifically, we investigated the effect of metal-infiltrated resists on electron-induced solubility by understanding the change of chemical bonds using an *in-situ* Fourier transform infrared spectroscopy (FTIR) equipped with electron gun capability. Each sample was exposed with electrons with 100 eV, which was similar energy of incident photons from EUV, and characterized the difference of chemical bonds before and after exposure. Based on these theoretical results, pure PMMA and metal infiltrated PMMA was exposed with a variable dose of electrons, followed the developing test with various solvent to investigate the effect of metal infiltration.

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EM2-5 About the Importance of Purge Time in Molecular Layer Deposition of Alucone Films

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The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). These alucone films tend to be porous in nature due to which the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an undesirable CVD component alongside MLD in the overall growth. We have investigated the MLD of alucone focusing on the effect of purge time of TMA on the growth kinetics. To avoid any negative impact of the CVD component on the deposition rate and the film's properties, we have also developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the CVD component in the growth. With an intention to improve the outgassing efficiency of TMA, the influence of purge gas flow on the CVD growth component has also been briefly investigated. Finally, we show that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration altogether and increase the deposition rate of alucone processes by at least an order of magnitude.

EM2-8 Low Temperature Alumina and Alucone Multistack by Ald for Flexible and Transparent Gas Barrier Layers

Shiv Bhudia, *N. Adjeroud, R. Leturq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Gas permeation barriers are widely employed in many technological applications. From medium barrier properties (Oxygen transmission rate, OTR ≈ 1 cc m^{-2} day^{-1} bar^{-1}; Water vapour transmission rate, WVTR ≈ 1 g $m^{-2}$$day^{-1}$) as in the food packaging industry. To very high barrier properties (OTR ≈ 10^{-5} cc m^{-2} day^{-1} bar^{-1} ; WVTR ≈ 1 g $m^{-2}$$day^{-1}$) such as in flexible organic opto-electronics. Here, it is even more critical to avoid the presence of water and oxygen in the active layer.

Atomic layer deposition (ALD) of amorphous alumina show very promising properties for passivation or encapsulation layer, for gas barrier layers. However, the deposition conditions usually require temperatures above 100 °C or highly oxidative conditions (ozone or oxygen plasma) to obtained reasonable deposition rates and high-density material. And due to its brittle nature, it limits the implementation on rigid or low flexibility substrates. A process for temperature sensitive substrates used in food packaging would be highly welcomed.

In this work, we combined amorphous alumina with alucone, in multi-stack structures on flexible PET substrate for food packaging. The inorganic alumina layer serves as gas barrier layer and the organic alucone layer decouples the adjacent alumina layers, thus avoiding direct passage of the permeant gas through pinholes.

By developing an in-house He permeation tester, we have investigated the physical diffusion of Hellium on these structures; and a method of extracting diffusivity and solubility from different substrate thickness is proposed. To further understand the morphology of these layers, we have simulated those structures using Finite Element Method (FEM).

EM2-11 Transport in Vapor Phase Infiltration Processes: Modeling and Measuring Competition between Reactions and Diffusion*, Emily McGuinness*, *Y. Ren, B. Jean, R. Lively, M. Losego,* Georgia Institute of Technology

Over the past decade, vapor phase infiltration (VPI) has emerged as a technique to create hybrid organic-inorganic materials with a wealth of industrially relevant applications. While the utility of VPI has become clear, the fundamental mechanisms that control the hybrid material structure (and therefore material properties) are complex and not well understood. In this presentation, a reactive-diffusion model is explored that provides insight into how the presence of reactions between polymers and metalorganic precursors modifies the transport behavior of the vapor phase metalorganic molecule through the material. This model is found to not only account for diffusion of the vapor phase metalorganic precursor within the polymer film, but also capture the reaction between the two phases, as well as associated reductions in diffusivity. For example, a hindering factor is established that accounts for the interference of chemically bound precursor with further diffusion of unbound precursor. This parameter captures the orders of magnitude reduction of out-diffusion coefficients as compared to in-diffusion coefficients observed in certain VPI systems. The model is shown to both qualitatively and quantitatively capture and predict VPI behaviors in an experimental case-study of the trimethylaluminum (TMA) / poly(methyl methacrylate) [PMMA] VPI system **(Figure 1)**. Parameters extracted from the model can be used to understand the fundamental thermodynamic and kinetic principles that underly the VPI process. For instance, the Damkohler number (a dimensionless value comparing the rate of diffusion to the rate of reaction in a system) for TMA / PMMA at 130˚C is found to be approximately 0.08. This value indicates that diffusion of TMA occurs faster than reactions between TMA and PMMA under these conditions. As a result of this, the TMA / PMMA system is able to exhibit high mass uptake in early times before hindering of the system sets in from the formation of bound precursor. Overall, this presentation will not only introduce a new model capable of capturing the complexities of VPI, but also provide guidelines and a case-study of its utility in experimental parameterization and prediction.

EM2-14 First Principles Study of Reactions in Hybrid Organic-Inorganic Films: The Impact of the Organic Reactant*, Arbresha Muriqi, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

The development of hybrid inorganic-organic films with well-controlled properties is vital for the future of nanotechnology for many applications. Molecular layer deposition (MLD) allows the deposition of hybrid films using sequential, self-limiting reactions, similar to ALD. In this study, we investigate the growth mechanism of different hybrid organic−inorganic thin films by using first principles density functional theory (DFT).

The prototype for MLD hybrid films are composed of thin films of aluminium alkoxides, known as ”alucones”. We investigated the MLD reaction productsbetween the post-TMA Monomethyl-Al_2O_3 ($Al-CH_3-Al_2O_3$) and Dimethyl-Al_2O_3 ($Al(CH_3)_2-Al_2O_3$) surface and diol organic precursors, including ethylene glycol (EG) as well as glycerol (GL). The results show that Al–O formation with release of methane is favorable for all diols. Interaction energies show that longer diols will not maintain an upright configuration compared to lying flat and participating in the “double reaction” where the two terminal –OH groups bind to surface TMA. A detailed comparison of ethylene glycol (EG) and glycerol (GL) precursors is presented to assist the interpretation of experimental findings regarding the differences in the hybrid films grown by EG and GL. EG and GL can lie flat and create double reactions through the two terminal hydroxyl groups. This phenomenon removes active hydroxyl sites for EG. For GL the third hydroxyl group is available and growth can proceed. This analysis shows the origin of differences in thickness of alucones found for EG and GL.

We also investigate the growth mechanism of magnesium containing hybrid films known as “magnesicone”from the reaction of EG and GL at MgCp-terminated MgO as a model system. Interaction energies show that while the ligand elimination process is favorable for both precursors, GL species prefers to lie in an upright position and EG prefers to orient in a flat configuration and interacts at the MgO surface, resulting in a thicker GL-based magnesicone compared to the EG-based magnesicone. This is consistent with the experimental findings for magnesicone growth using these precursors.

Finally we study the growth of titanium-containing hybrid organic−inorganic films known as “titanicones”. using titanium tetrachloride ($TiCl_4$) or tetrakisdimethylamido ($Ti(TDMA)_4$) as metal source and ethylene glycol (EG) or glycerol (GL) as organic reactants. This investigation contributes to the understanding of growth process of EG and GL based titanicones at different surfaces and is valuable in supporting experimental data on titanicone film growth.

Emerging Materials
Room On Demand - Session EM3
Atomic Layer Epitaxy and Doping

EM3-1 Low-Temperature Dopant-Assisted Crystallization of HfO_2 Thin Films*, Theodosia Gougousi,* Department of Physics, UMBC

We have studied the thermal ALD of HfO_2 on native and chemical oxide GaAs(100) surfaces using various aklylamide precursors. Bright field and HRTEM data for ***as-prepared*** 12 -36 nm HfO_2 films deposited on native oxide GaAs(100) at 250°C from tetrakis ethymethylamino hafnium (TEMAHf) and H_2O shows that the films are polycrystalline. These films contain several large grains of the order of the film thickness and numerous small crystallites (Figure 1). To clarify the role of the GaAs(100) substrate in the observed HfO_2 film structure an additional set of films was grown on GaAs(100) surfaces that were chemically oxidized. The chemical oxide layer thickness was measured at ~4.6 nm more than twice the thickness of the native oxides. GaAs chemical oxides are similar in composition to the native oxides. HfO_2 films with thickness ~6 nm deposited on the chemical oxide GaAs(100) surfaces are also polycrystalline while ~2 nm of the chemical oxide layer is still detectable at the interface (Figure 2). The presence of the chemical oxide at the interface precludes the direct contact of the HfO_2 layer with the GaAs substrate. Normally, HfO_2 films of such low thickness remain amorphous even after they are subjected to thermal treatment. One of the highlights of alkylamide HfO_2 ALD processes on III-V substrates is the so-called interface cleaning reaction that leads to the gradual consumption of the surface native oxides and results in the formation of a sharp HfO_2/III-V semiconductor interface. We have shown that this interface cleaning reaction is accomplished because the surface native oxides transport to the surface of the growing ALD oxide layer where they react with the precursor to form volatile byproducts that are removed. So, at any point during the ALD process there is mixing of the various III-V oxides in the film but because of the removal mechanism the final ALD film has very low impurity content. We hypothesize that the native oxides lead to the stabilization of the various HfO_2 polymorphs during low temperature thermal atomic layer deposition allowing control of the film microstructure via the deposition process.

Emerging Materials
Room On Demand - Session EM8
Nanolaminates

EM8-1 Properties of Atomic Layer Deposited ZrO_2 or Fe_2O_3 Based Multilayers*, Helina Seemen, K. Kukli, A. Tamm,* University of Tartu, Estonia

Research devoted to the achievement of multiferroic thin-film materials is actual, and the task itself has appeared to be quite challenging. At the same time, it could also be rewarding in the case of success due to prospective applications as these materials are useful for non-volatile memories and electromagnetic sensor materials. In this study, five-layer nanolaminates consisting of alternately deposited ZrO_2 and Co_3O_4 layers, and two-layer structures consisting of Fe_2O_3 film and BiOCl nanoflakes were deposited to explore their potential advanced magnetic properties [1, 2]. The main goal was to achieve a ferromagnetic-like response with the measurable coercivity values getting as high as ten kOe. The Fe_2O_3-BiOCl combination was partly selected due to the possible formation of bismuth ferrite, which is known to be one of the most promising multiferroic materials, at the interfaces.

The ZrO_2-Co_3O_4 5-layer nanolaminates were grown by atomic layer deposition at 300 ℃ from $ZrCl_4$ and $Co(acac)_3$ as metal precursors and O_3 as the oxygen precursor. The Fe_2O_3-BiOCl two-layer thin-film structures were deposited from $FeCl_3$, $BiCl_3$ and H_2O at 375 ℃.

The results showed that the multilayers of both studies were crystallized in the as-deposited state. In the ZrO_2-Co_3O_4 5-layer nanolaminates, the cubic and monoclinic ZrO_2 phases and cubic Co_3O_4 phase were present. Orthorhombic ε-Fe_2O_3 and tetragonal BiOCl phases were detected in the case of Fe_2O_3-BiOCl two-layer thin-film structures. In Table I, selected multilayer structures, their total thicknesses and measured coercivity values are presented. Magnetic hysteresis loops showed nonlinear and saturative magnetization and measurable coercivity, indicating ferromagnetic-like behaviour at room temperature. The highest coercivity value measured was 9757 Oe (776.4 kA/m), which characterized one particular Fe_2O_3-BiOCl two-layer thin-film structure (Table I). SEM images of this type of multilayer structure are displayed in Figure 1. In the case of the ZrO_2-Co_3O_4 nanolaminates, the coercivity values were 21 and 32 Oe (1.7 to 2.5 kA/m) (Table I). All five layers of the nanolaminates were clearly distinguishable (Figure 2).

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EM8-2 Evaluation of the Near-Zero Temperature Coefficient of Resistivity (Nz-TCR) of ALD $TiSi_xN$ Films*, **Corbin Feit**, S. Berriel ,* University of Central Florida*; A. Dhamdhere, B. Nie, H. Cho, H. Kim, S. Chugh, S. Rathi, N. Mukherjee,* Eugenus, Inc.*; P. Banerjee,* University of Central Florida

Atomic Layer Deposition (ALD) of ternary $TiSi_xN$ leads to nanocomposites of metallic TiN atomically mixed with insulating Si_3N_4. Formulating $TiSi_xN$ films with various Ti:Si ratios lead to the emergence of a temperature regime where resistivity is independent of thermal drift, denoted as near-zero temperature coefficient of resistivity (nz-TCR). Further, the ease with which nanocomposites of $TiSi_xN$ can be deposited using ALD offer precise tunability in Ti:Si ratio, thickness, mass density, crystallinity and electrical properties.

Recently, our group explored $TiSi_xN$ films deposited using a Eugenus® 300 mm commercial QXP mini-batch system by modulating the ratio of Ti and Si precursors with NH_3 as a co-reactant.Si-content was varied from 0 at % (pure TiN) to 24.2 at % Si while maintaining thickness ~ 140 nm. The X-ray reflectivity and grazing incidence X-ray diffraction measurements showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si-fraction. Spectroscopic ellipsometry revealed the optical constants, composition, and electrical resistivities and were supported by X-ray photoelectron spectroscopy and electrical measurements. Room-temperature resistivity measurements show an increase in film resistivity with increasing at % Si. Temperature-dependent Van der Pauw measurements found a nz-TCR of -23 ppm K^{-1} in the temperature range of 298 K – 398 K and at 3.4 at % Si content.

We have now discovered that an at % Si = 3.0% induces a nz-TCR of -5.7 ppm K^{-1} from 80 K – 420 K – one of the best reported nz-TCR values for ALD thin films. Fine tuning the at % Si in $TiSi_xN$ films, possible only via ALD, significantly elongated the temperature window of nz-TCR behavior. Mapping the local conductivity of individual grains through conductive atomic force microscopy (c-AFM) indicated higher resistance at the grain boundaries. The local composition at the grain boundaries may play a major role in determining the nz-TCR behavior of $TiSi_xN$ films. In addition, variable temperature Hall effect measurements were performed to provide deeper insights into the nz-TCR mechanism, decoupling carrier concentration from carrier mobility effects while determining film resistivity.

Compared to other nz-TCR films, which are deposited using physical vapor deposition techniques, ALD based nz-TCR films presents a unique synthesis platform for interconnect technology in topologically complex, 3D devices, circuits and sensors that undergo large temperature variation during operation but need to maintain stability in their electrical characteristics.

Emerging Materials
Room On Demand - Session EM9
Ternary and Quaternary Materials

EM9-1 Substitutional W Doping of MoS_2 for Threshold Voltage Control of Field Effect Transistor*, **Hwi Yoon**, W. Woo, I. Sohn, Y. Lee, S. Seo, S. Cheong, H. Kim, H. Kim,* Yonsei University, Korea

Two dimensional (2D) layered transition metal dichalcogenides (TMDCs) have attracted great attention owing to its excellent properties such as superior mechanical flexibility, transparency thermal stability, and compatibility to silicon CMOS processes. In particular, molybdenum disulfide (MoS_2) has been extensively studied in recent years. MoS_2 has been considered as attractive channel material for electronic switch device applications in the form of field-effect transistors (FETs) due to superior electrical properties such as thickness-dependent bandgap, high field-effect mobility, high current on/off ratio (>10^8), nearly ideal subthreshold swing (SS). Despite all the advantages of MoS_2 as a promising candidate to replace silicon in such devices, large variations in the threshold voltage (V_{th}) of FET makes difficult it in practical application. The Vth of silicon-based semiconductor technology at the 22 nm technology node is 0.289 V for high performance logic and 0.413 V for low operating power logic. In contrast, values of Vth of back-gated MoS_2 FETs being reported vary from −30 V to 40 V. In the case of Si-based FET, V_{th} can be easily tuned by doping through ion implantation. However, this method cannot be applied to MoS_2 because energetic processes such as implantation, plasma easily cause damage to MoS_2. In this study, we developed one-step doping process during chemical vapor deposition (CVD) of MoS_2. electrical properties such as carrier density, bandgap and chemical composition tuned according to dopant concentration. In addition, V_{th} modulation of MoS_2 was carried out by using substitutional doping of W. V_{th} of MoS_2 FET has decreased by more than 10 V after doping.

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EM9-2 Atomic Layer Deposition of $CuSn_XS_Y$ from Low-Cost Precursors and Its Optical and Electrical Characteristics*, **Jakub Ostapko**, G. Kołodziej, M. Wlazło,* CBRTP - Research and Development Center of Technology for Industry, Poland*; Z. Starowicz,* Institute of Metallurgy and Materials Science, Poland*; G. Putynkowski,* CBRTP - Research and Development Center of Technology for Industry, Poland

Metal sulfides are of high importance for thin-film photovoltaics applications. Some of the most widely studied structures belong to the quaternary compounds group and play the role of solar cell absorber: CIGS ($CuIn_{(1-x)}Ga_xSe_2$) and CZTS (Cu_2ZnSnS_4). The ternary structure, Cu_2SnS_3 (CTS),[1] has been reported in the literature as a simplified and potential absorber material. Ordinarily, methods different than ALD are used for their synthesis. In case of record CIGS[2] (23.35% efficiency) and CZTS[3] (12.6%) cells, DC sputtering and solution approaches were used, respectively.

ALD is dedicated to the preparation of uniform thin films. There are a few reports in the literature concerning ALD synthesis of technologically important ternary[4–8] and quaternary[9] sulfides. The ALD synthesis of sulfide-based absorbers is hindered by some limitations: precursor chemical compatibility, including reactivity with the sulfur precursor, parasitic reactions, and the limited volatility of precursors. These limitations are reflected by low growth per ALD cycle. The other aspects that limit ALD utility are high moisture and oxygen sensitivity, and high prices of commercially available metal precursors.

In this study, a new process of ALD deposition of ternary sulfide $CuSn_xS_y$ is presented. The material has been prepared using affordable copper and tin precursors. This is contrasted with the reported ALD processes, which use expensive organometallic reactants as sources of Cu and Sn. The synthesis has been carried out at low temperature. Films of $CuSn_xS_y$ varying in stoichiometry were synthesized. Film morphology, including cross-section imaging, was provided by SEM analysis. The elemental composition was determined by EDS. The results of optical (UV-vis spectroscopy) and electrical measurements (Hall effect, four-point probe) are presented and discussed in the context of the photovoltaic application of ALD synthesized $CuSn_xS_y$ films.

The obtained results highlight the versatility of the ALD technique and provide an example of a cost-effective synthesis of thin-film absorber material.

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Nanostructure Synthesis and Fabrication
Room On Demand - Session NS2
Nanotubes, Nanowires, Nanopores

NS2-1 Atomic Layer Deposition for Modification of Various 1D Nanomaterials*, R. Zazpe, H. Sopha, M. Motola,* Uni Pardubice, Czechia*; M. Rihova,* Brno University of Technology, Czechia*; **Jan Macak**,* Uni Pardubice, Czechia

One-dimensional nanomaterials – materials with one dimension outside the nanoscale, further noted as 1D NMs – represent a class of very important nanomaterials with continuously increasing importance. Due to their intrinsic features, unique properties and diversity of functionalities, they count among the most widely studied materials nowadays. While considerable research efforts have been spent to synthesize various 1D NMs (e.g. nanopores, nanotubes or nanofibers), limited efforts have been devoted to surface modification and property tailoring of these materials.

However, it is their surface that comes into direct contact with various media (air, gases, liquids, solids) and influences the reactivity, stability and biocompatibility of these materials. The surface and aspect ratio (defined as their diameter to length ratio) influence the performance of these materials in various applications. Considering these facts, it is more relevant to tailor the surface of these materials and to be able to influence their properties and reactivity at the nanoscale, rather than to deal with tailoring their own bulk material composition.

The focus of this presentation is on the modification of two types of 1D nanomaterials – nanotubes and nanofibers. Numerous techniques can be utilized for this purpose, such as for example wet chemical or physical deposition techniques. However, it is only the Atomic Layer Deposition (ALD) that is capable of really uniform and homogenous coating of these 1D nanomaterials, in particular those of very high-aspect ratio.

The presentation will be mainly focused on modification of TiO_2 nanotube layers and various nanofibers of different aspect ratios via ALD.

Experimental details and some very recent application examples [1-9] and structural characterizations of these modified materials will be discussed.

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Nanostructure Synthesis and Fabrication
Room On Demand - Session NS3
2D Nanomaterials by ALD (including Transition Metal Dichalcogenides)

NS3-1 2D Core-Shell Quantum Dots Grown by ALD*, **Jeff Schulpen**, M. Verheijen, E. Kessels, V. Vandalon, A. Bol,* Eindhoven University of Technology, Netherlands

Two-dimensional transition metal dichalcogenides (e.g. MoS_2, WS_2) have fascinating optical and electronic properties that make them promising materials for use in next-generation devices. In particular, 2D quantum dots (i.e. nanoparticles of 2D materials) have received great interest in recent years for their effectiveness in catalysis as well as opto-electronic and energy-storage applications [1]. Furthermore, the versatility of 2D materials is greatly enhanced by the fact that they can be assembled with atomically sharp interfaces, resulting in heterostructures that benefit from the combined functionality of multiple 2D materials as well as completely new material properties [2]. Applying heterostructure methods to 2D quantum dots could result in core-shell nanoparticles which combine the useful properties of 2D quantum dots with the versatility of heterostructures. However, little is known about such structures, as most of the literature is aimed at single-material quantum dots.

In this work, we show that 2D monolayer core-shell quantum dots can be grown by atomic layer deposition. Using a supercycle approach, we grow crystalline nano-scale monolayer flakes of MoS2 which are subsequently epitaxially bordered by WS_2. This is achieved by exploiting the reactive edge sites of these materials, by switching from MoS_2 to WS_2 deposition before a closed monolayer is formed. Notably, this method can be extended to the growth of more elaborate structures (e.g. core-shell-shell), whereby the diameter of the core and shell(s) can be straightforwardly and accurately controlled through the number of ALD cycles. In practice, the size control of the grown core-shell structures is limited by the nucleation density of the ALD process, which is linked to the density of reactive sites on the substrate [3,4]. In order to enable the growth of larger and more elaborate structures, we employ strategies to reduce the nucleation density. The growth is investigated in-situ using spectroscopic ellipsometry, and the grown structures are characterized by AFM and TEM, as well as Raman and PL spectroscopy. We expect our technique of growing 2D core-shell quantum dots to extend to other 2D material systems, thereby establishing an important new method of tailoring the properties of 2D quantum dots for applications in catalysis, opto-electronics and energy-storage.

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NS3-2 2D Molybdenum Dichalcogenides Family by Atomic Layer Deposition*, **Raul Zazpe**,* University of Pardubice, Czech Republic*; R. Krumpolec,* Masaryk University, Czech Republic*; J. Charvot, L. Hromadko,* University of Pardubice, Czech Republic*; H. Sopha,* University of Pardubice, Czech Republic , Czechia*; M. Motola, F. Bures, J. Macak,* University of Pardubice, Czech Republic

2D semiconductor transition metal dichalcogenides have attracted considerable attention due to their layered structure, suitable band gap, electrochemically active unsaturated edges and relatively good stability against photocorrosion. These properties result promising for different applications including, Li-ion batteries, photocatalysis and hydrogen evolution reaction (HER). Apart from the widely studied 2D MoS2, 2D selenide and telluride equivalents, MoSe2 and MoTe2, have recently gained considerable interest due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap as compared to MoS2, high surface area and close to zero Gibbs free energy edges for hydrogen adsorption. Unlike sulfide dichalcogenides, the lack of Se and Te precursors have prevented the synthesis of selenide and telluride dichalcogenides by ALD. In order to surpass such impediment, we present a set of novel in-house synthesized Se and Te compounds, which were successfully combined with commercial Mo precursor to synthesize MoSe2 and MoTe2 by ALD [1-5]. The as-deposited ALD MoSe2 and MoTe2 on substrates of different nature were extensively characterized by different techniques, which confirmed the chemical composition and revealed the growth of 2D flaky nano-crystalline MoSe2 and MoTe2. In parallel, MoSe2 and MoTe2@TiO2 nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the MoSe2 and MoTe2 photo- and electrocatalytic properties. TNTs act as excellent photoactive supporting material providing a high surface area, unique directionality for charge separation, and highly effective charge collection.

The presentation will introduce and describe the synthesis of the 2D Mo dichalcogenide family, the corresponding physical and electrochemical characterization and encouraging results obtained in HER [4,5], photocatalysis [4-6] and Li-ion batteries [7].

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NS3-3 Atomic Layer Deposition of Ultrathin Tungsten Oxide Films for 2D WS_2 Synthesis*, **Maxim Kozodaev**, R. Romanov, A. Markeev,* Moscow Institute of Physics and Technology, Russian Federation

Tungsten oxide attracts great attention as a functional layer of electrochromic [1] or resistive memory devices [2], but also as a source for the synthesis of two-dimensional ultrathin WS_2 nanosheets, which can serve as a channel material in the post-silicon FET technology [3]. In this regard, ALD utilization for the tungsten oxide growth is highly preferable since it allows the best thickness control and reproducibility over other deposition techniques, which is crucial for mass-production. Previously it has been reported that radical-enhanced ALD also allows precise oxygen deficiency control in WO_x films [4].

In this work, we modify the previously reported $WH_2(Cp)_2$-based ALD process by the oxygen source exchange to ozone. This process showed a clear saturation behavior on both reactants, good deposition uniformity, and higher oxygen deficiency level, which was monitored by in-situ X-Ray photoelectron spectroscopy to exclude film degradation under ambient conditions. The V_o presence was concluded from the visible electronic states formation in the bandgap, an increase in the concentrations of tungsten in the W5+ state and oxygen in the non-lattice state. An increase in the V_o concentration was accompanied by a significant film resistivity decrease and an abrupt change in the crystalline structure, which was revealed by XRD analysis. The early stages of the suggested WO_x ALD process were studied by angle-resolved XPS and the moment of film continuity was determined. The subsequent sulfurization allowed its' effective conversion to WS_2 nanosheets with the terrace-terminated structure. Recently it was shown that preliminary seed WO_x film hydrogen treatment allowed to significantly change WS_2 morphology and improve its' electrical quality [5]. Noteworthy, exactly ultrathin WS_2 layers are of particular interest, therefore, the seed WO_x thickness influence on the resulting WS_2 morphology was also investigated. In particular, such a technique allowed us to obtain the continuous WS_2 nanosheets with a thickness down to 3-4 monolayers. The obtained results expand the opportunities horizon of the 2D materials by the possibility of a fab-oriented production technique.

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NS3-6 Wafer-Scale Synthesis of Transition Metal Dichalcogenide Thin Films by ALD-Based Technique Towards Nanoelectronics and Optoelectronics Applications*, **Hao Zhu**, Z. Gu, T. Zhang, H. Liu, L. Chen, L. Ji, Q. Sun,* Fudan University, China

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are attracting growing interests in recent years due to their unique electronic properties even with thickness at atomic scale. Though tremendous progress has been made in the understanding and implementation of the physical properties of TMDs in advanced micro-/nanoelectronic devices through conventional fabrication methods like mechanical exfoliation or chemical vapor deposition (CVD), the large-scale device integration for system-level applications have been severely bottlenecked by the lack of effective synthesis approaches to achieve wafer-scale, uniform, crystalline and stoichiometric TMD films.

Atomic layer deposition (ALD) is a surface-controlled film fabrication and can provide a promising route towards the synthesis of high-quality TMD thin films since the ALD approach follows the layer-by-layer deposition mechanism. As compared to other synthetic methods like CVD, ALD can enable precise thickness control on atomic scale and excellent film uniformity as well as good stoichiometry and crystallinity with proper annealing steps. Here, we have developed ALD-based synthesis approaches to prepare wafer-scale MoS_2 and WS_2 TMD thin films. Non-toxic $MoCl_5$, WCl_5 and hexamethyldisilathiane (HMDST) are used as precursors. Film characterizations have confirmed the wafer-level uniformity and good crystallinity by annealing in sulfur atmosphere. The field-effect transistor (FET) device arrays fabricated on the wafer-scale TMD film have shown excellent homogeneity in electrical performance, which provides good platform for further integration. In our work, we have fabricated optoelectronic device arrays as well as inverter, NAND, NOR, AND, and OR logic gates which have shown robust and repeatable logic functions. This has paves solid basis for the system and circuit-level applications.

It should also be noted that we have been designing and optimizing a high-temperature ALD process to grow crystalline TMD thin films eliminating the high-temperature annealing step in the previous flow. Preliminary experimental results have been achieved demonstrating satisfactory film quality, and the FET devices fabricated on it can exhibit repeatable switching performance with on/off ratio over 10^3. We believe that this can be a more encouraging synthetic method to prepare wafer-scale TMD thin films for practical electronic applications.

Nanostructure Synthesis and Fabrication
Room On Demand - Session NS4
ALD on 2D Related Materials and Devices

NS4-1 Recovery Enhancement of Al_2O_3 Functionalized MoS_2 Gas sensor by Atomic Layer Deposition*, **Inkyu Sohn**, S. Wi, Y. Kim, M. Kim, H. Yoon, S. Jung, H. Kim,* Yonsei University, Korea

Two-dimensional (2D) transition metal dichalcogenides (TMDs) which possess large surface-to-volume ratio have been widely used for room temperature gas sensing applications. [1] However, due to its intrinsic defect or vacancies on TMD surface, incomplete recovery of TMD gas sensors hinder the realization of reliable and repeatable use of 2D TMD gas sensors. [2] Here, we demonstrate improvement of recovery rate of TMD gas sensors by covering TMD surfaces' defect or vacancies with Al_2O_3 using atomic layer deposition. Raman, AFM, XPS data have been showed. Especially, SEM data have showed that Al_2O_3 is partially covered on grain boundaries or defects of MoS_2 which is favorable for enhancing recovery performance of TMD gas sensors. The pristine MoS_2 gas sensors show 74 % of recovery rate in the case of NO_2 sensing. However, the recovery rate of the Al_2O_3 functionalized MoS_2 gas sensors improved up to 96 %. Our proposed method shows promising strategy for improving recovery rate of 2D TMD gas sensors.

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Nanostructure Synthesis and Fabrication
Room On Demand - Session NS5
ALD on Polymer Materials

NS5-1 ALD of In_2O_3 in PMMA: Resolving the Atomic Structure of Sequential Infiltration Synthesized Clusters*, X. He, R. Waldman, S. Darling, D. Tiede, **Alex Martinson**,* Argonne National Laboratory

Sequential infiltration synthesis (SIS) is a route to the precision deposition of inorganic solids in analogy to ALD but occurs within a soft material template. SIS has enabled exquisite nanoscale morphological complexity in several oxides through selective nucleation in block copolymers templates. However, the earliest stages of SIS growth remain unresolved, including the atomic structure of nuclei and the evolution of local coordination environments, before and after polymer template removal. We employed In K-edge extended X-ray absorption fine structure and atomic pair distribution function analysis of high-energy X-ray scattering to unravel the structural evolution of InO_xH_y clusters inside a poly(methyl methacrylate) (PMMA) host matrix. Early SIS cycles result in InO_xH_y cluster growth with high aspect ratio, followed by the formation of a three-dimensional network with additional SIS cycles. That the atomic structures of the InO_xH_y clusters can be modeled as multinuclear clusters with bonding patterns related to those in In_2O_3 and $In(OH)_3$ crystal structures suggests that SIS may be an efficient route to 3D arrays of discrete-atom-number clusters. Annealing the mixed inorganic/polymer films in air removes the PMMA template and consolidates the as-grown clusters into cubic In_2O_3 nanocrystals that form porous In_2O_3 solids, the morphology of which also depends on cycle number.

NS5-2 Understanding and Controlling Polymer-Organometallic Precursor Interactions in Sequential Infiltration Synthesis*, Inbal Weisbord*, *N. Shomrat, R. Azoulay, A. Kaushansky, T. Segal-Peretz,* Technion - Israel Institute of Technology, Israel

With the emergence of sequential infiltration synthesis (SIS) as a prominent method for growth of inorganic materials inside polymeric structures, it becomes essential to understand the mechanism of precursor diffusion and reaction inside polymers, in order to expand the scope of SIS, and allow growth in thicker specimen, under more economic conditions.

This study uses a combination of density functional theory calculations and *in-situ* microgravimetric measurements to shed light on the equilibrium interaction between the polymers polymethyl methacrylate (PMMA) and poly-2-vinyl pyridine (P2VP) and the organometallic precursor trimethyl aluminum (TMA). The relationship between temperature, diffusion and reaction is probed, to reveal that while diffusion increases with temperature, the strength of reaction decreases. In low temperatures the strong reaction forms a low diffusivity region at the top of the film and inhibits further growth. At high temperatures, diffusion is high, but poor reaction strength prevents the precursor from binding in the film. The study finds the balance point, which is the optimum point that maximizes both factors, for each polymer. SIS dynamics, prior to reaching equilibrium, are probed using *in-situ* microgravimetric measurement, as well, enabling precise control over AlO_x growth in PMMA and P2VP, as corroborated by electron microscopy. The knowledge gained from this thorough analysis is then used to design a process of TMA growth inside self-assembled polystyrene-*block*-P2VP in a manner that both preserves the self-assembly and allows for significant AlO_{x-} growth.

NS5-3 Atomic Layer Deposition of Al_2O_3 and TiO_2 on Polydimethylsiloxane*, Albert Santoso*, *B. van den Berg, V. van Steijn, J. van Ommen,* TU Delft, Netherlands

Atomic layer deposition (ALD) on polymeric substrates is attracting increasing attention due to potential applications in OLEDs, food packing, and biomaterials. By depositing a very thin film of metal oxide, the surface properties, such as wettability, and overall performance of the material can be adjusted without losing the unique bulk properties. However, due to the inherent porous structure and competing precursor reaction on the polymeric branch, the deposition of metal oxide on polymers does not follow the ideal ALD mechanism. The subsurface growth and minimal surface diffusion lead to a non-conformal layer and subsequently different final properties. In this study, we focus on the surface modification of polydimethylsiloxane (PDMS) which is widely used material to fabricate microreactor and lab-on-a-chip devices. We have investigated the use of ALD of alumina and titania on PDMS using two different ALD reactors (vacuum and atmospheric) at various operating conditions (temperature, substrate pretreatment). X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used for material characterization, while contact angle hysteresis measurements have been used for approximating the surface energy stability over time. Results indicate that at high temperature (120°C), micro-sized cracks and buckles are formed due to a difference in thermal expansion coefficient of metal oxide and PDMS, which density are reduced as the temperature goes down. When comparing the effect of oxidizing precursor, thermal ALD of metal oxide on PDMS leads to severe infiltration of precursors, and subsequently subsurface growth up to micron range, which have little influence on the surface wetting property. On the other hand, low temperature plasma-assisted vacuum ALD results into a surface growth, suggesting the growth kinetic is more dominant than the precursor diffusion, although nano-sized cracks and non-conformity were also still observed, which end up with certain hydrophobic recovery. The recovery rate is reduced by using atmospheric ALD. Further XPS analysis shows that there are some elements of ligand components from the precursor that may remain trapped due to incomplete purging, which might act as a pinhole-filler in subsurface infiltration and surface layer growth, leading to higher stability in surface energy. This study gives insight in utilizing thin films grown by non-ideal ALD as buffer layers for robust modification of polymeric substrates, which could be applied in not only controlling fluid behavior but also obtaining the desired surface property.

NS5-6 Modified 3D Printed Architectures: Effects of Coating and Infiltration by Alumina on ABS*, Atilla Varga*, *B. Nwokolo, P. Gordon, S. Barry,* Carleton University, Canada

In recent years 3D printing has gained enormous popularity thanks to its affordability, accessibility, ease of use, and the ability to easily employ a variety of polymer materials. These potential polymer substrates are highly tunable in flexibility and strength which make them the ideal for printing filaments, they can incorporate metal powders, wood fibers, carbon fibers, etc.[1] The integration of 3D printing and industrial nanoscale processes such as ALD will have a significant impact in the development of advanced 3D printed architectures leading to a wide array of applications.

ALD modification of 3D printed structure can be applied in nanoparticle growth, which has applications in low-cost high surface area catalysts. Both thin film coatings as well as precursor infiltration have already been studied in chemical resistant polymer coatings, conductive polymer networks, and various other applications of interest in electronics, sustainable materials and manufactured products.[2]

Previously ALD has been used to deposit alumina thin films on various types of polymers.[3] This work will expand the deposition of alumina onto 3D printed, of one of the most commonly available 3D printed substrates: acetonitrile butadiene styrene (ABS). The observed effects of either coating or infiltration of alumina on the polymers' physical properties such as melting point, glass transition temperature, thermal decomposition, and conductivity will be studied. The effects of coating versus infiltration will be contrasted to demonstrate the extent to which these characteristics can be tuned.

Scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) will be used to examine the modified polymer structures (Figure 1). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and conductivity probe measurements will be used to observe the physical property changes of the treated polymer compared to the untreated.

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Nanostructure Synthesis and Fabrication
Room On Demand - Session NS6

Nanostructures Synthesis and Fabrication Poster Session

NS6-1 Synthesis of Silicon Carbide Thin Films by Post-Processing of Molecular Layer Deposition (Mld) Polyamide Films on Silicon*, Rustam Amashaev*, Dagestan State University, Russian Federation*; I. Abdulagatov,* Dagestan State University , Russian Federation

Silicon carbide (SiC) is a technologically important material that has many industrial applications. SiC films on Si substrates have been used to fabricate transistors, optical waveguides and components for quantum computers. In addition, SiC films have been used to obtain another technologically significant material – graphene. There are several primary ways to deposit SiC films: physical and chemical vapor deposition (PVD and CVD). Although these methods can deposit good quality films, they cannot fulfill all the stringent requirements, in terms of film conformality, thickness control, and cost effectiveness, needed to manufacture modern microelectronics devises.

In this work, we studied alternative approach for controlled synthesis of epitaxial quality SiC thin film. This method based on pyrolysis of MLD polyamide film deposited on single crystal Si substrate (see Fig.) [1]. MLD allows to deposit highly conformal organic thin film with precise thickness control. Consequently, it might be possible by controlling the parameters of the initial MLD film accurately control the thickness and uniformity of the SiC film.

MLD polyamide films were deposited at 120 ^{o}C by thermally stimulated surface reactions between trimesoyl chloride (TMC) and 1,2-ethylenediamine (EDA). *In situ* QCM monitoring of the MLD process showed linear increase in mass with the number of cycles. The polyamide film growth rate on Si(111) was 18.5 Å/cycle. After deposition, pyrolysis was conducted at temperatures between 1000 and 1300 ^{o}C and pressure of ~10^{-7} Torr. Number of *ex situ* characterization methods, such as, scanning electron microscopy (SEM), x-ray diffraction (XRD), Raman, energy-dispersive x-ray spectroscopy (EDX), and reflection high-energy electron diffraction (RHEED) were employed to analyze samples after pyrolysis. These techniques confirmed that after heat treatment single crystal b-SiC (3C-SiC) thin films have been synthesized.

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NS6-2 Fabrication of Free-standing Three-dimensional Structures by Spatial Atomic Layer Printing*, **Philipp Wiesner**, I. Kundrata,* ATLANT, Germany*; S. Tymek, M. Barr,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; M. Plakhotnyuk,* ATLANT, Denmark*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

One of the most common processes to produce microelectronics is optical lithography. It combines deposition by different thin film techniques including CVD or ALD with etching of defined structures using masks.This multistep procedure is time-consuming and wasteful of material. Spatial Atomic Layer Printing offers an alternative for the direct production of defined structures and therefore for components in microelectronics.

In this study, free-standing three-dimensional bridges are produced using the atomic layer 3D printer, developed by ATLANT 3D Nanosystems, that provides direct atomic layer writing process. For this purpose, two crossing lines are deposited from a support and a print material, subsequently the support material is removed via wet chemistry etching processes. To ensure an intact bridge, different material combinations of platinum, titanium dioxide, silicon dioxide and zinc oxide are used and post-processed by different etching methods. In particular, the materials used and the type of etching play an important role in producing freely standing structures. Important aspects in the preparation of the component are the influence of the etchant on the materials, the temperature used, the surface tensions of the etchant and the cleaning agent as well as the mechanical stress during the process.

The most promising material combination during the test series is a printing material of titanium dioxide deposited with TTIP and H2O and a support material of zinc oxide deposited with diethylzinc and H2O. To ensure the gentlest possible etching process, the support material is removed by vapor etching using hydrochloric acid and the sample is cleaned by immersion in a mixture of 90 % ethanol and 10 % water. As a result, most of the titanium dioxide bridges are retained and can be characterized (see Figure 1). The samples produced still have cracks and spalling on the bridges, but it can be demonstrated that the ATLANT 3D Nanosystems atomic layer 3D printing process can be used for the direct deposition of free-standing three-dimensional structures that can be further used to fabricate components in microelectronics.

NS6-5 Al_2O_3 ALD Buffer Layers for Epitaxial Growth of Boron Nitride Beyond the Self-Termination Limit*, **Mateusz Wlazło**,* CBRTP - Research and Development Center of Technology for Industry, Poland*; P. Caban,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland*; G. Kołodziej ,* CBRTP - Research and Development Center of Technology for Industry, Poland*; P. Michałowski ,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

The Metalorganic Chemical Vapor Deposition (MOCVD) is a recognized method for the growth of BN epitaxial layers. The important progress in the understanding of the MOCVD growth was achieved when it was demonstrated that the growth mode could be changed from 3D to self-terminated one under high reactor pressure and increased in V/III ratio. It is known that the main problem in the deposition of BN layers is that in self-terminated mode the total layer thickness does not exceed 2nm.In this presentation structural properties of BN layers grown directly on the Al2O3, or using Al2O3 buffer layers made by ALD were investigated. Application of one or two buffer layers was investigated as well as Al2O3 buffer properties. The measurements techniques used for investigation of the grown films concentrated on AFM however involved SIMS, ATR spectroscopy, XRR, Raman. The motivation behind this work is to show directions towards the increase of the total layer thickness.

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