ALD Applications
Room Van Rysselberghe - Session AA-MoM2
ALD for Solar Energy

Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., Paul Poodt, Holst Centre / TNO

10:45am **AA-MoM2-1 Atomic Layer Deposition for Silicon-Perovskite Tandem Cells*, Bart Macco*, *N. Phung, E. Kessels, M. Creatore,* Eindhoven University of Technology, Netherlands **INVITED**

Solar cells are one of the pillars of the energy transition, where cells based on silicon wafers dominate this market of currently over 200 gigawatts per year. Though not widely known, ALD is now omnipresent in these silicon cells, where on the order of 10 billion wafers are coated with Al_2O_3 passivation layers per year, often using batch or spatial ALD.[1]

While silicon solar cells will dominate the market for the foreseeable future, the anticipated “next big thing” are so-called monolithic tandem solar cells which combine a silicon bottom cell and a perovskite top cell. These tandem cells have skyrocketed in efficiency to almost 30% (compared to 26.7% for silicon only), and have an incredible momentum both in R&D and pilot production.

These tandems cells are highly relying on functional thin films and as such this offers many more opportunities for ALD. Materials “beyond simple ALD Al_2O_3” are needed, including passivation, charge transport and buffer layers as well as tunnel recombination junctions with transparent conductive oxides. At the same time, the application has stringent demands such as extremely low cost, pinhole-free conformal films to avoid electrical shunts and often the need for processing on sensitive perovskite (e.g. max. temperature of ~100 ^oC). As will become clear, the distinct merits of ALD such as soft deposition, relatively low-temperature processing, conformality and excellent control over doping and stoichiometry are highly relevant in this field. This will be highlighted through selected case studies. These include ALD SnO_2, a well-established buffer layer which is present in most *(if not all)* recent record tandem cells, as well as recent innovations from our group being ALD NiO hole-selective contacts on the perovskite side [2] and ZnO:Al-based electron contacts on the silicon side.[3]

Finally, I would like to thank the whole PERCSpective consortium for their contributions.

[1] B. Macco, “What can Atomic Layer Deposition do for solar cells?,” *AtomicLimits.com*, 2019. https://www.atomiclimits.com/2019/10/15/what-can-atomic-layer-deposition-do-for-solar-cells-a-few-afterthoughts-from-my-ald-conference-tutorial/.

[2] N. Phung *et al.*, “Enhanced Self-Assembled Monolayer Surface Coverage by ALD NiO in p-i-n Perovskite Solar Cells,” *ACS Appl. Mater. Interfaces*, 2021, doi: 10.1021/acsami.1c15860.

[3] B. Macco *et al.*, “Atomic-layer-deposited Al-doped zinc oxide as a passivating conductive contacting layer for n+-doped surfaces in silicon solar cells,” *Sol. Energy Mater. Sol. Cells*, vol. 233, no. September, p. 111386, Dec. 2021, doi: 10.1016/j.solmat.2021.111386.

11:15am **AA-MoM2-3 ALD Al_2O_3/SiO_x Multilayers for c-Si Surface Passivation: Modification of Interface Properties by Voltage Stress and Plasma Treatments*, Armin Richter*, *H. Patel, C. Reichel, P. Masuch, J. Benick, S. Glunz,* Fraunhofer ISE, Germany

Al_2O_3 is one of the most effective dielectric surface passivation layers for silicon solar cells. Due to the high amount of negative fixed charges, it is particularly suited for the passivation of p-type Si surfaces. However, other surface passivation schemes indicated recently that there is still room for improvement which becomes more and more important with increasing solar cell performance.

In contrast to single layers, multilayers with thicknesses of only a few nanometers of the individual layers open the opportunity to modify material properties on a nanometer scale. Multilayers of Al_2O_3 and SiO_2, for instance, have been studied recently for the application in MOSFETs because they allow to tune the flat-band voltage shift simply by varying the number of single layers in the multilayer. The origin of this voltage shift are dipoles, which are formed only at the SiO_2/Al_2O_3 interface with one polarity but not at the Al_2O_3/SiO_2 interface with the opposite polarity.

In this work we investigate systematically if such Al_2O_3/SiO_2multilayers are also beneficial for Si surface passivation. We used ALD to prepare the multilayer because of its ultimate deposition control and being at the same time industrially relevant. With CV measurements we studied the interface characteristics (interface defect density D_{it} and total effective fixed charge density Q_{tot}) to gain insights into the electronic properties of the multilayers.

Our results reveal that by varying, for instance, the number of layers in the stack or the deposition and post deposition anneal temperature, the surface passivation of the multilayers is very similar to that of Al_2O_3 single layers but not significantly improved. In fact, we found that Q_{tot} of the multilayers is actually even lower than that of the Al_2O_3 single layers. We studied further the influence of voltage stress. We found that it strongly effects Q_{tot} for both the multilayers and Al_2O_3 single layers and that voltage stress of the right polarity results in a significantly increase of Q_{tot}. However, too high voltage stress deteriorates D_{it}, i.e. the chemical passivation.

In addition, we studied also whether in-situ plasma treatments during the deposition of the multilayer effects its electronic properties. We found that especially H plasmas after the SiO_2 deposition results in a quite substantially improved surface passivation, significantly better than that of the Al_2O_3 single layer. A detailed analysis of the interface properties will be provided in the final paper. As such, our results indicate a promising way of improving the Si surface passivation. However, our results can be also interesting for other semiconductor devices.

11:30am **AA-MoM2-4 Atomic Layer Deposition of Aluminium Doped $Zn_{1-x}Mg_xO$ as Transparent Conducting Films for Photovoltaics*, Poorani Gnanasambandan*, *N. Adjeroud, R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

We investigate atomic layer deposited aluminium doped zinc magnesium oxide films with varying Al content as transparent conducting films with tunable bandgap. While Aluminium doping of zinc oxide increases the electrical conductivity, it decreases the transmission due to absorption close to the band edge [1].On the other hand, with addition of Mg, the optical properties and bandgap of ZnO can be tuned making them well-suited for photovoltaic applications [2].

Most previous studies on aluminium doped zinc magnesium oxide (Al:ZMO) involved sputtering. While ALD has been used to investigate both aluminium doped zinc oxide (AZO) and magnesium doped zinc oxide (ZMO) [2][3], studies on Al:ZMO were limited to few ratios [4]. Also, the ALD studies fixed the Al-Zn doping concentration around 3% and varied the Mg doping. We aim to increase the electrical conductivity and tune the bandgap by varying both Al and Mg doping concentration.

Optimizing a quaternary process by mixing three binary ALD process involves immense challenges [5]. We achieve high degree of control on composition by optimizing the growth conditions with supercycle parameters such as pulse ratios and bilayer period. With the advantage of precise composition control, we study ALD grown Al doped $Zn_{1-x}Mg_xO$ with x varying from 0.2 to 0.3 and varying aluminium doping concentrations from underdoped to over doped cases. We elucidate the effect of doping on the band alignment, electrical and optical properties.

[1].Zhang, Wu, et al. "Tailoring of optical and electrical properties of transparent and conductive Al-doped ZnO films by adjustment of Al concentration." Materials Science in Semiconductor Processing 74 (2018): 147-153.

[2]. Törndahl, T., et al. ‘Atomic Layer Deposition of Zn1−xMgxO Buffer Layers for Cu (In,Ga)Se2 Solar Cells’. Progress in Photovoltaics: Research and applications 15.3 (2007): 225-235.

[3]. Peng, Qing, Anil U. Mane, and Jeffrey W. Elam. "Nanometer-Thick Mg x Zn (1–x) O Ternary Films for Photovoltaics." ACS Applied Nano Materials 3.8 (2020): 7732-7742.

[4]. Fleischer, Karsten, et al. Aluminium Doped Zn 1 − x Mg x O – a Transparent Conducting Oxide with Tunable Optical and Electrical Properties. Applied Physics Letters 101.12 (2012): 121918.

[5]. Mackus, Adriaan JM, et al. "Synthesis of doped, ternary, and quaternary materials by atomic layer deposition: a review." *Chemistry of Materials* 31.4 (2018): 1142-1183.

11:45am **AA-MoM2-5 An in-Situ Infrared Spectroscopy Study on the Influence of ALD SnO_2 on Formamidinium-Based Metal Halide Perovskite*, A.E.A. (Andrea) Bracesco*, *J. Jansen, W. Kessels,* Eindhoven University of Technology, Netherlands*; V. Zardetto,* Solliance Solar Research, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The conversion efficiency of metal halide perovskite solar cells (PSCs) has reached 25.7%.[1] This record was achieved through engineering of the opto-

electronic properties of the absorber and charge-selective and efficient interfaces between charge transport layer (CTLs) and the absorber. Recently, the focus has shifted towards the replacement of organic CTLs, often leading to parasitic absorption and long-term device instability. Metal oxides prepared by gas phase deposition methods, such as ALD, are prime candidates. The ALD merit of control over film stoichiometry, conformality and uniformity has led to several applications in PSCs. In this respect, ALD SnO_2, in combination with fullerene-based electron transport layers (ETLs), is the state-of-the art in p-i-n PSCs, imparting thermal and environmental stability to the device.[2] However, when attempting to replace the fullerene ETLs by ALD SnO_2 processed directly on the perovskite absorber, a poor device performance is observed, due to severe chemical changes imparted to the inorganic fraction of the perovskite, as previous XPS studies showed.[3,4]

In this contribution, we shift the focus of the investigation on the organic fraction of the perovskite absorber, specifically on the formamidinium cation (FA) in a $CsFAPb(I,Br)_3$ perovskite. By adopting in situ IR spectroscopy, we evaluate the effect that ALD processing conditions, such as substrate temperature, vacuum, and exposure to half and full ALD SnO_2 cycles (tetrakis(dimethylamido)-Sn(IV) (TDMA-Sn) and H_2O), have on FA IR spectral features. We observe that the cation is not affected by vacuum (10^{-5} mbar) and exposure to water half-cycles. Instead, prolonged exposure to a temperature range of 50-100°C (standard SnO_2 processing temperature on perovskite with/out the fullerene-based ETL) leads to the loss of N-H stretching modes. We speculate that FA deprotonates into formamidine, which is then released from the surface. Lastly, we report that the loss of FA, is also detected when the perovskite surface is exposed to a 500 ms pulse of TDMA-Sn. Moreover, the precursor-perovskite surface interaction leads to the formation of sym-triazine, i.e. a decomposition product of formamidine, which becomes trapped at the perovskite/SnO_2 interface. These studies enable to decouple the several effects of direct ALD processing on perovskite and highlight the major role played by the Sn-precursor in affecting the perovskite surface chemistry.

[1]H. Min et al., Nature,598, 444–450, 2021

[2]V. Zardetto et al., Sustainable Energy Fuels, 1, 30-55, 2017

[3]A. F. Palmstrom et al., Adv. Energy Mater., 8-23, 1800591, 2018

[4]A.E.A. Bracesco et al., JVSTA, 38, 063206, 2020

ALD Applications
Room Van Rysselberghe - Session AA1-MoA

ALD for Catalysis

Moderator: Ashley R. Bielinski, Argonne National Laboratory

1:30pm **AA1-MoA-1 ALD Preparation of TiO_2-MnO_x/SiO_2 Catalyst for Selective Catalytic Reduction of Nitrogen Oxides***, **Saeed Saedy,*** Delft University of Technology, Netherlands*; D. Kazimierz ,* Paul Scherrer Institut, Switzerland*; D. Urbanas,* Vilnius Gediminas Technical University, Lithuania*; D. Ferri,* Paul Scherrer Institut, Switzerland*; J. van Ommen,* Delft University of Technology, Netherlands

The most efficient NO_x abatement process is the selective catalytic reduction using NH_3 (NO_x NH_3-SCR). The commercial V-based NH_3-SCR catalysts have a narrow high-temperature operational window of 350-450°C; this requires installing the catalyst bed before desulfurization and dust removal units, which initiates catalyst deactivation. To avoid this, the SCR unit is currently being placed in the so-called tail-end configuration, which results in exhaust gases temperature below the operational window of the commercial catalysts. Manganese oxide (MnO_x) catalysts show superior NH_3-SCR activity at low temperatures (LT). The various oxidation states (Mn^{2+},Mn^{3+},and Mn^{4+}) of MnO_x, are known to play an essential role in the LT activity of MnO_x catalysts; hence, the existence of multiple oxidation states of Mn is pivotal for its SCR activity. On the other hand, the crystalline MnO_x does not contribute effectively to NH_3-SCR; thus, the dispersion of MnO_x strongly affects SCR activity. The routine catalyst synthesis methods like precipitation impregnation, and sol-gel, are less suitable for preparing MnO_x SCR catalysts since they often require high-temperature post-treatments, which increase the crystallinity of particles and decrease dispersion.

Atomic layer deposition (ALD) offers a reliable LT coating method, with subnanometer control over the process. ALD makes it possible to obtain metal oxide nano-coatings at temperatures significantly lower than conventional methods. In this work, we have employed fluidized bed ALD to deposit highly dispersed MnO_x on SiO_2 for LT NH_3-SCR catalysis. The ultra-fine MnO_x NPs were grown on SiO_2 at 150°C and 1 bar. Additionally, we deposited TiO_2 on ALD prepared MnO_x/SiO_2 to increase the acidity of the catalyst, which is crucial for NH_3 activation during the SCR process. The XPS analysis revealed three oxidation states of Mn^{2+}, Mn^{3+},and Mn^{4+} in these samples, which are essential for NO_x-SCR. Also, powder XRD could not detect any crystalline phases of MnO_x, suggesting that ALD synthesis avoided the crystalline MnO_x; consistently, the MnO_x NPs were scarcely observable using TEM, demonstrating extreme dispersion of MnO_x over SiO_2. NH_3 temperature-programed desorption analysis demonstrated that the acidity of the MnO_x/SiO_2 sample is significantly increased after TiO_2 ALD, increasing the NH_3 activation on TiO_2-MnO_x/SiO_2. The obtained TiO_2-MnO_x/SiO_2 with such characteristics provide a promising catalyst for low-temperature selective catalytic reduction of nitrogen oxides. Accordingly, the catalytic activity evaluation showed~85% NO conversion for the TiO_2-MnO_x/SiO_2 sample, while the MnO_x/SiO_2 sample showed a NO conversion of~30%.

1:45pm **AA1-MoA-2 Unravelling the Mechanism of Electrochemical Activation of ALD Cobalt Phosphate by Digital Control Over Its Chemical Composition***, G. van Straaten, R. Zhang, E. Kessels,* Eindhoven University of Technology, The Netherlands*; R. van de Sanden, M. Tsampas,* Dutch Institute for Fundamental Energy Research, Netherlands*; **Mariadriana Creatore,*** Eindhoven University of Technology, The Netherlands

Storage of electricity into molecules is the most viable answer to the intermittency of renewable sources. In this respect, H_2O splitting to H_2 and O_2 is key to enable the usage of H_2 as fuel for transport, as well as building block together with CO for the electrosynthesis of hydrocarbons. For the O_2 evolution half reaction (OER), cobalt phosphate (CoPi) is interesting because it behaves as bulk electro-catalyst, with electrochemically active Co^{3+} centers. In parallel with others [1], we have demonstrated the synthesis of amorphous CoPi films by ALD [2]. CoPi was prepared by combining ALD of CoO_x from cobaltocene and O_2 plasma, with cycles of trimethyl phosphate and O_2 plasma, according to an ABCD scheme [2,3]. We have also shown that ALD CoPi films are characterized by OER performances beyond those achieved by traditional electro-deposited films [3].

In the present contribution we focus on the mechanism behind the enhancement of the catalytic activity of ALD CoPi when tuning the Co-to-P ratio in the film. We show that CoPi films progressively undergo activation under alkaline conditions (ph=8-14) with increasing number of cyclic voltammetry (CV) cycles. During this activation process induced by the infiltration of the electrolyte in the bulk of the film, the current density increases in parallel with the leaching of phosphorus out of the electro-catalyst and the shift of the oxidation state of cobalt from Co^{2+} to Co^{3+} [4]. In parallel, the film undergoes a change in morphology upon activation. CV analysis and Rutherford backscattering measurements indicate that after activation, as much as 22% of all cobalt content in the film becomes accessible to the electrolyte and is activated. The electrochemical surface area (ECSA), i.e. the surface area accessible to promote H_2O splitting, increases up to a factor of 30, accompanied by a current density of 5 mA/cm^2. The increase in ECSA is strongly dependent on the composition of the pristine CoPi films: while the above-mentioned 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 4. We find that for all investigated Co-to-P ratios, the electrochemical activity scales linearly with ECSA upon activation. It can be concluded that the digital control over the chemical composition of CoPi offers a novel merit to ALD: unravelling the mechanism behind CoPi electrochemical activation.

[1] J. Ronge et al., Nanoscale Adv. 1, 4166 (2019)

[2]V. Di Palma et al., Electrochem. Commun. 98, 73 (2019)

[3] V. Di Palma et al., J. Vac. Sci. Technol. 38, 022416 (2020)

[4] R. Zhang et al., ACS Catal.11, 2774 (2021)

2:00pm **AA1-MoA-3 Increasing ALD Complexity: How to Transform Ternary Oxide Films Into Tunable Bimetallic Thin Films and Nanoparticles***, J. Feng, **Matthias Filez,** M. Minjauw, E. Solano, C. Detavernier, J. Dendooven,* Ghent University, Belgium

ALD of ternary compounds ($A_mB_nC_o$) typically combines two binary ALD processes, each consisting of a metal precursor source and a co-reactant. Recently, however, we have demonstrated that ternary compounds, in casu $MRuO_x$ (M = Al, Pt), can be deposited using a single binary ALD process, thus reducing deposition complexity.[1] During such process, metal-organic precursors ($MeCpPtMe_3$ and TMA) are combined with RuO_4, the latter functioning both as metal source and co-reactant which combusts organic ligands. Yet, such multi-constituent co-reactant limits deposition to ternary compounds, such as $MRuO_x$, while often metallic MRu films or nanoparticles (NPs) are desired. Herein, we show that by increasing the complexity of the original $MRuO_x$ process by adding extra 'functionalities', such as reduction or even etching steps, bimetallic films and NPs can be deposited with full thickness and compositional control. This approach therefore significantly extends the applicability of the original process toward bimetallic compounds.

We first show that ALD of bimetallic PdRu films can be achieved by inserting a RuO_4 step in the $Pd(hfac)_2$ / H_2-plasma (H_2*) process, leading to a three-step $Pd(hfac)_2$ / RuO_4 / H_2* process with a high growth per cycle of 0.19 nm/cycle.[1, 2] Herein, RuO_4 acts both as an oxidizing agent and a Ru source, while H_2* reduces the surface. Thin films resulting from this process are Ru-rich, and we show that the Pd content can be increased by not including the RuO_4 step in every cycle, thus decreasing the incidence rate of the RuO_4 step in the ALD process (Fig. 1).

Next, by replacing part of the RuO_4 units in the three-step process by O_2*, the morphology of the PdRu is transformed from thin films to bimetallic nanoparticles (BMNPs, Fig. 2). This change of morphology is attributed to the etching of the deposited Ru as volatile RuO_4 during the O_2* steps. In situ grazing-incidence small-angle X-ray scattering and X-ray fluorescence revealed that the composition and size of the BMNPs can be adjusted independently by changing the proportion of RuO_4 versus O_2* pulses in the sequence, and the total number of ALD cycles, respectively. Finally, grazing-incidence wide-angle X-ray scattering and electron energy loss spectroscopy revealed that the RuPd BMNPs are crystalline, and Ru and Pd intimately mixed, suggesting the formation of solid-solution RuPd nanoalloys.

[1]Minjauw, M. M. et al. (2022).*Dalt. Trans.* Advance Article (DOI: 10.1039/D1DT03543F)

[2]Feng, J. Y. et al. (2020).*Phys. Chem. Chem. Phys.*, **22**, 9124–9136.

2:15pm **AA1-MoA-4 Tunable TiO_2-BN-Pd Nanofibers by Combining Electrospinning and Atomic Layer Deposition to Enhance Photodegradation of Acetaminophen**, ***Syreina Alsayegh,*** Institut Européen des Memabranes, France*; M. Bechelany,* Institut Européen des Membranes, France*; F. TANOS,* Institut Européen des membranes, France*; A. NADA, G. LESAGE, F. Zaviska,* Institut Européen des Membranes, France*; M. Weber,* Laboratoire des Matériaux et du Génie Physique LMGP , France

The demand for fresh and clean water sources increases globally, and there is a need to develop novel routes to eliminate micropollutants and other harmful species from water. Photocatalysis is a promising alternative green technology that has shown great performance in the degradation of persistent pollutants. Titanium dioxide is the most used catalyst owing to his attractive physico-chemical properties, but this semiconductor presents limitations in the photocatalysis process due to the high band gap and the fast recombination of the photogenerated carriers. Herein, a novel photocatalyst has been developed, based on titanium dioxide nanofibers (TiO_2 NFs) synthesized by electrospinning. The TiO_2 NFs were coated by atomic layer deposition (ALD) to grow boron nitride (BN) and palladium (Pd) on their surface. The UV-Vis spectroscopy measurements confirmed the increase of the band gap and the extension of the spectral response to the visible range. The obtained TiO_2/BN/Pd nanofibers were then tested for photocatalysis, and showed a drastic increase of acetaminophen (ACT) degradation (>90%), compared to only 20% degradation obtained with pure TiO_2 after 4h of visible light irradiation. The high photocatalytic activity was attributed to the good dispersion of Pd NPs on TiO_2-BN nanofibers, leading to a higher transfer of photoexcited charges carriers and a decrease of photogenerated electron-holes recombination. To confirm their reusability, recycling tests on the hybrid photocatalyst TiO_2/BN/Pd have been performed, showing a good stability over 5 cycles under UV and Visible light. Moreover, toxicity testsas well as quenching tests were carried out to check the toxicity in the formation of byproductsand to determine active species responsible for the degradation. The results presented in this work demonstrate the potential of TiO_2/BN/Pd nanomaterials, and open new prospects for the preparation of tunable photocatalysts.

Keywords: TiO_2-BN-Pd nanocomposites; nanofibers, electrospinning; atomic layer deposition; photocatalysis; acetaminophen

2:30pm **AA1-MoA-5 Ultra-Low Dimensional Ir-Ru Thin-Film by Atomic Layer Deposition on Porous Titanium Felt Substrate for Electrochemical Water Splitting Application**, ***Rahul Ramesh,*** *N. Park, T. Cheon,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)*; M. Byeon, T. Hong,* Busan Center, Korea Basic Science Institute, Korea (Republic of)*; S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Iridium (Ir) and ruthenium (Ru) are crucial ingredient in various applications, and their proper utilization is essential due to the extreme rarity of those elements. For example, in the case of electrocatalysis, only the surface participate in the reaction, and whatever lies beneath (within the nanoparticle or thin film) are un-utilized. Therefore, fabrication of Ir/Ru thin-film with high uniformity and conformality onto high surface area porous substrate is beneficial to reduce the metal content and increase its utilization. Atomic layer deposition (ALD) can be used to deposit uniform and conformal films with precise thickness control. In this study, we report the fabrication of ultra-low dimension (~5 nm) Ir-Ru thin film on to porous Ti felt substrate using a sequential approach with two precious metal ALD processes. The nano-secondary ion mass spectrometer depth-profiling (Nano-SIMS) results confirm the homogeneous, conformal and uniform growth of Ir-Ru thin film as predicted from the ideal ALD growth characteristic and XTEM on Si substrate. The electrochemical performance of Ir-Ru nanolayer electrode towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are evaluated in an acid electrolyte (0.5 M H_2SO_4). The Ru film shows the highest onset for HER (-112 mV), the Ir (5 nm) and Ir-Ru (5 nm) has an HER onset potential of ~-50 mV. In the case of the OER voltammogram, all the electrodes with precious metal films show the current due to OER. Contrary to the HER, here Ru shows the highest activity both in terms of OER onset potential and the overpotential at a specific current density; noteworthy the slightly better activity of 5 nm Ir film is attributed to the Ru nucleation layer (~2 nm) deposited on to the Ti substrate for uniform deposition of Ir, since, there is a huge nucleation delay for Ir ALD on Ti-based substrate. The stability of the film is characterized by chrono-potentiometric stability analysis for 24 hours at an OER current density of 10 mA cm^{-2}. As expected the Ru film is very unstable during OER and complete dissolution of 5 nm film happens at around ~4 hour of operation. However, the Ir-Ru (5 nm) display enhanced stability and is attributed to the inclusion of Ir. In conclusion, ALD can be used as an efficient technique to coat ultra-low dimension Ir-Ru thin film/nano-materials on to porous substrate with precise thickness control and high conformality, which is beneficial in terms of utilization and cost-effectiveness of electrocatalyst.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2021R1A2C1007601 and 2021M3H4A3A02099209.

2:45pm **AA1-MoA-6 Influence of Co/Ni Ratio on OER-catalytic Performance of Atomic Layer Deposited Nickel Cobalt Oxide**, ***Renee van Limpt,*** Eindhoven University of Technology, Netherlands*; M. Lavorenti, M. Tsampas,* Dutch Institute for Fundamental Energy Research, Netherlands*; A. Creatore,* Eindhoven University of Technology, Netherlands

A promising approach to answer the challenge of intermittency of renewable sources such as wind and solar energy, is to store green electricity into H_2 via H_2O electrolysis. Sustainable electrolysis can be achieved, for example, under alkaline conditions, with the sluggish oxygen evolution reaction (OER) representing the main limitation. Mixed oxides of the earth-abundant cobalt and nickel are considered promising OER electrocatalysts. Cobalt nickel oxide ($Co_xNi_{1-x}O_y$) can adopt both the Co_3O_4 spinel and the NiO rock-salt structure depending on the cobalt concentration. The present study aims at exploring the effect of cobalt concentration in $Co_xNi_{1-x}O_y$ on the OER catalytic activity to expand on previous literature studies which are either limited to single phase structures[1, 2] or disregard the effect of bulk (film thickness >5 nm) effects[3].

Atomic layer deposition (ALD) offers the opportunity to tune the stoichiometry and therefore the structure of $Co_xNi_{1-x}O_y$. This work therefore employs plasma-enhanced ALD by combining a cobalt cyclopentadienyl ($Co(Cp)_2$)[4] based process for CoO_x with a nickel methylcyclopentadienyl ($Ni(MeCp)_2$) process[5] for NiO_x. Energy Dispersive X-ray mapping shows no variation in elemental composition, indicating that nickel intermixes with cobalt to form an alloy. X-ray spectroscopy (XPS) furthermore reveals the presence of mixed Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} valence states, with an increase in the Ni^{3+}-to-Ni^{2+} ratio for increasing cobalt concentrations. Preliminary x-ray diffraction measurements furthermore suggest a transition from rock-salt to spinel phase with increasing cobalt concentration, indicating that nickel occupies the octahedral sites in the spinel structure at high cobalt concentrations. The OER activity of $Co_xNi_{1-x}O_y$ films (~30 nm) is determined by cyclic voltammetry (CV) in 1M KOH. The current density at 1.8 V vs RHE increases whilst the onset potential decreases, with a decrease in cobalt concentration in the film. An increased number of CV cycles leads to an increase in the current density, suggesting the activation of the bulk of the electrocatalyst. After CV, XPS reveals a dominant Ni^{3+} oxidation state in the film and an increase in oxygen concentration and hydroxide phase. These results indicate that the rock-salt phase is favourable for OER, implying that further research should focus on low cobalt- content $Co_xNi_{1-x}O_y$.

[1]R. N. Singh et al., *Electrochim. Acta*, 2000.

[2]A. Asho etl al., *Int. J. Hydrogen Energy*, 2019.

[3]L. Trotochaud et al., *J. Am. Chem. Soc.*, 2012.

[4]M. E. Donders et al. *J. Electrochem. Soc.*, 2011.

[5]D. Koushik *et al.*, *J. Mater. Chem. C*, 2019.

3:00pm **AA1-MoA-7 Fundamental Studies of s-ALD Grown Iridium Thin Films on Planar Substrates for Acidic Water Splitting**, *J. Shen ,* TNO-Holst Centre, Netherlands*; P. Shirvanian,* TNO-STIP, Netherlands*; E. Balder,* TNO-Holst Centre, Netherlands*; B. van Dijk,* TNO-STIP, Netherlands*; N. Huijssen, A. Bronneberg, P. Poodt,* ***Mahmoud Ameen,*** TNO-Holst Centre, Netherlands

One of our greatest challenges for the upcoming decades is the transition to a sustainable way of generating, storing, and converting energy. Green hydrogen produced by PEM Water Electrolyzers (PEMWE's) is part of the solution, but still faces several challenges. Among the major challenges towards widespread adoption and commercialization of PEMWE's are the cost, performance, and durability of iridium (Ir) material as used to catalyze the oxygen evolution reaction (OER) [1]. Sluggish OER kinetics and ensuing large overpotential above the thermodynamic equilibrium level required to drive the reaction will inevitably result in PEMWE inefficiency along with high catalyst loadings. It has previously been demonstrated that atomic layer deposition (ALD) can be used to deposit high quality and stable electrocatalyst layers with a low Ir loading [2], but the low deposition rate of ALD limits up-scaling for mass production. Spatial atomic layer deposition (sALD) has emerged as a viable tool for the atomically precise design and

synthesis of materials with high deposition rates on both large substrates (square meters) and roll-to-roll [3].

Herein, we present an atmospheric-pressure spatial ALD process of Ir/IrO_x ultra-thin films on flat substrates. We investigate the temperature window of the ALD process down to 80 degrees. We study the growth characteristics as well as the thin film properties using ellipsometry, inductively coupled plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy (XPS) and grazing incidence X-ray diffraction (GIXRD). Furthermore, we evaluate the OER catalytic behaviour and durability using rotating disc electrode (RDE). Our study sheds light on structure, thickness, and morphology of Ir deposits and corresponding OER catalytic properties. The findings will pave the way towards identifying optimal catalytic system with the promise of ultra-low Ir loading at high OER performances.

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3:15pm **AA1-MoA-8 Functionalization of MoS_2 With Noble Metal by Atomic Layer Deposition for Hydrogen Evolution Reaction***, **JungYub Lee**, J. Kim, I. Sohn, S. Chung, H. Kim,* School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)

Hydrogen is a good, sustainable alternative energy that can replace fossil fuels that cause air pollution and global warming. To produce hydrogen, electrochemical water splitting is the promising sustainable method without producing carbon containing pollutant.[1]

Platinum has been widely used for hydrogen evolution reaction(HER) for its high performance compared to other materials. However, platinum faces the problem in commercial use because of its low cost efficiency. In order to replace platinum, Transition Metal DichalCogenides(TMDCs) have been actively researched, which have a high surface-to-volume ratio and provide a sufficient number of active sites.[2] To further enhance the HER performance of TMDCs, many research has focused on the structure of TMDCs, defect engineering and heterojunction with graphene. However, this research will highlight the signficance of Pt and its better performance than those methods. To prove, this study will funtionalize TMDCs with the very small amount of noble metals, including Pt and Ru. Atomic Layer Deposition(ALD) will be a key technique to control the amount of noble metals and synthesize the uniform, conformal TMDCs on graphite foil.

Here we prepared catalyst using the noble metal functionalized MoS_2 synthesized on graphite foil by ALD. Various experimental methods were performed to analyze film growth characteristics including X-ray photoelectron spectroscopy (XPS) , Raman spectroscopy, Scanning Electron Microscope (SEM), X-ray diffraction and etc. The electrochemical properties of HER catalyst show high exchange current density and low Tafel slope compared with ALD MoS_2 film.

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ALD Applications
Room Van Rysselberghe - Session AA2-MoA

ALD for Energy Storage

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, Philippe Vereecken, IMEC, Belgium

4:00pm **AA2-MoA-11 Conversion Reactions and Redox Changes on the Surface of Lithium-Ion Battery Cathode Materials during Chemical Vapor Treatment for ALD***, P. Darapaneni, A. Mane, Z. Hood, **Jeffrey Elam**,* Argonne National Laboratory

Atomic layer deposition (ALD) has emerged as a promising technology for applying ultrathin protective coatings on lithium-ion battery (LIB) cathode surfaces to improve their cycling stability. While there have been numerous reports evaluating the electrochemical performance of these surface-modified cathode materials, the chemical changes induced on the surface of the cathode materials by the ALD coatings and the individual ALD precursors are not fully studied. We performed a systematic investigation to understand the interfacial changes of 12 different cathode materials upon coating with aluminum oxide (Al_2O_3) using trimethyl aluminum (TMA) and H_2O, and aluminum fluoride (AlF_3) using TMA and hydrogen fluoride pyridine (HFPy). We also explored the effects of the individual TMA and HFPy precursors on the cathode surfaces.The surface composition and microstructure of these cathode materials, which range from simple transition metal oxides (e.g., NiO and MnO) to complex multi-element cathode materials (e.g., $LiNi_xMn_{1-x-y}Co_yO_2$, NMC), were studied via X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM). The XPS measurements reveal that the transition metals in the cathode materials undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, XPS and STEM measurements show the conversion of surface carbonate species to the corresponding metal fluorides upon HF exposure.This conversion reaction is self-limiting but extends hundreds of nanometers below the surface in the case of Li_2CO_3.ALD and chemical vapor treatment provide new avenues to systematically control the interface of the cathode materials in LIBs that are not possible by conventional coating methods.

4:15pm **AA2-MoA-12 Titanium Carboxylate MLD Hybrid Films as Protective Coatings for Lithium-Ion Batteries***, **Sofie S. T. Vandenbroucke**, L. Henderick,* Ghent University, Belgium*; L. De Taeye,* IMEC, Belgium*; J. Li,* Ghent University, Belgium*; K. Jans, P. Vereecken,* IMEC, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Li-ion battery cathodes age due to phenomena as transition metal dissolution, electrolyte oxidation and volume expansion. [Vetter J., et al. (2005) *J. power sources*] A protective coating can be applied to the cathode's surface to avoid direct contact with the electrolyte. Many studies have shown the protective effect of conformal and pinhole-free ALD films. However, inorganic films are rigid and may crack upon volume expansion of the cathode. [Ban C., et al. (2016) *Adv. Mat. Int.]* MLD offers the same deposition controllability as ALD but can be used to deposit hybrid films that are more flexible to accommodate potential volume expansions. In this work, titanium carboxylate thin films are deposited using tetrakis(dimethylamido)titanium (TDMAT) and various dicarboxylic acid precursors: oxalic acid, malonic acid, succinic acid, glutaric acid and 3,6-dioxaoctanedioic acid (Fig 1). The latter containing two ethylene oxide units per molecule, potentially increasing the Li-ion conductivity. [Xue Z., et al. (2015) *J. Mat. Chem. A*]

The growth of the titanium carboxylate thin films is studied using in situ ellipsometry at a substrate temperature of 100 and 160 °C. Only the TDMAT/oxalic acid process displays good saturation behavior, while a parasitic CVD component is present during the TDMAT pulse for the other processes (Fig 1). FTIR and XPS confirm the successful deposition of titanium carboxylate films. The films are found to be stable in air up to 50 days in contrast to many metalcone MLD films. In addition, FTIR, XRR and XRF measurements show that the films remain intact upon immersion into the liquid electrolyte used for electrochemical characterization (1 M $LiClO_4$ in propylene carbonate).

The electrochemical properties of 5 nm films grown with TDMAT/oxalic acid, TDMAT/3,6-dioxaoctanedioic acid and TDMAT/glycerol (titanicone film [Van de Kerckhove K., et al. (2016)*Dalton Trans.*]), respectively, are compared on top of three ideal electrode systems: anatase TiO_2, TiN and $LiMnO_2$ (LMO). The titanium carboxylate films have little to no effect on the Li-ion kinetics of the TiO_2 electrode system. This is in contrast to the titanicone film displaying a detrimental effect on the kinetics. All films

effectively suppress electrolyte oxidation when exposing the TiN electrode system to elevated potentials (Fig 2). On the LMO electrode an activation step is necessary for all films, after which a good Li-ion mobility through the titanium carboxylate films is observed without the severe irreversible reactions detected for the titanicone film. Overall, the titanium carboxylate films seem promising candidates as flexible coatings to protect Li-ion battery cathodes.

4:30pm **AA2-MoA-13 Surface Coating and Grain Boundary Engineering of NMC811 Materials for Next-Generation Li-Ion Batteries***, **Zahra Ahaliabadeh**, V. Miikkulainen,* Aalto University, Finland*; M. Mäntymäki,* University of Helsinki, Finland*; T. Kallio,* Aalto University, Finland

Nickel-rich layered metal oxide $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) is one of the most promising cathode materials owing to its high energy density. Therefore, these cathode materials have a prime interest for the electric vehicle battery manufacturers to build next-generation lithium-ion batteries. However, NMC811 suffers from several irreversible parasitic reactions and interfacial/structural instability that lead to severe capacity fading and impedance buildup during prolonged cycling. Thin surface protection films coated on the electrode material are feasible and effective solutions to solve these challenges. It can mitigate degradative chemomechanical reactions at the electrode–electrolyte interphase, which helps to increase cycling stability. However, most of the coatings including metal oxide may impede the diffusion of lithium ions, and therefore, limit the performance of the cathode material. Thus, the physical and chemical properties of the coating materials are effectual factors in providing optimized protection for the electrode materials. In our research, we worked on the deposition of Li-containing metal oxide layers with different thicknesses through atomic layer deposition method, on the surface of NMC811. Lithium titanate, was coated on the NMC811 electrode and found to be effective in the elimination of surface impurities and reducing the capacity loss. Characterization analysis such as Scanning electron microscopy (SEM-EDS) and Transmission Electron Microscopy (TEM) results confirmed the diffusion of the coating in to the NMC grain boundaries which helped to stabilize the structure, as evidenced by providing longer lifetime with an 87% capacity retention after 100 cycles. Besides the characterization and electrochemical analysis, *in-situ* dilatometry and *in-situ* XRD analysis showed irreversible volume change for NMC811 bare while it was mostly reversible for the coated ones during the cycling. The results revealed that the dilation behavior of the electrode, resulting in crack formation and particle degradation, has been significantly suppressed for the coated samples. The ability of the coatings to mitigate the electrode degradation mechanisms, provides insight into a method to enhance the performance of Ni-rich positive electrode materials. To enhance the electrochemical performance of NMC811 under high-voltage ranges, the addition of organic molecule to the coating is suggested. Such a hybrid coating layer can combine the functions of promoting Li^+ ion transport, as well as enhancing the electrical conductivity due to the coating structural properties. This new coating is under examination and its results will be demonstrated later.

4:45pm **AA2-MoA-14 Hybrid Inorganic/Organic Polycarbonate Track-Etched Membranes With Tunable Pore Size and Surface Functionality for Redox Flow Batteries***, **Rajesh Pathak**,* Applied Materials Division, Argonne National Laboratory*; X. Fang,* Indiana University−Purdue University Indianapolis*; R. Shevate, V. Rozyyev, A. Mane,* Applied Materials Division, Argonne National Laboratory*; X. Wei,* Indiana University−Purdue University Indianapolis*; Z. Xia,* Argonne Center for Molecular Engineering, Argonne National Laboratory*; L. Zhang,* Chemical Science and Engineering Division, Argonne National Laboratory*; S. Babinec,* Argonne Collaborative Center for Energy Storage Science (ACCESS), Argonne National Laboratory*; S. Darling,* Argonne Center for Molecular Engineering, Argonne National Laboratory*; J. Elam,* Applied Materials Division, Argonne National Laboratory

Abstract

Redox flow batteries (RFBs) hold great promise for the stationary storage of renewable energy from solar and wind power because they combine high safety with low cost, and because they decouple energy density and power density through the physical separation of redox-active species in liquid solutions. Despite these positive attributes, the high cost of existing RFBs limits their widescale deployment in the electric power grid.Significant cost reduction is possible if new technologies for the manufacture of low-cost, highly selective ion transport membranes can be developed.In this study, we explore isoporous polycarbonate track-etched membranes (PCTEs) modified by sequential infiltration synthesis (SIS) and atomic layer deposition (ALD) to tune the pore size and pore surface chemistry as a platform for developing low-cost, high-performance RFB membranes. We perform a systematic study of Al_2O_3 SIS and ALD in PCTE to establish the range of conditions that yield precise control over the membrane pore size.Next, we functionalize the pore wall surfaces with a variety of ALD metal oxide coatings to tune the surface charge and hydrophilicity.Finally, we evaluate the membrane properties and performance in aqueous organic redox flow batteries with (ferrocenylmethyl)trimethylammonium chloride (FcNCl)/methyl viologen (MV) in noncorrosive neutral sodium chloride supporting electrolyte to establish structure-function-property relationships.We anticipate that this work will provide a pathway to developing low-cost inorganic/organic ion transport membranes for RFB applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; neutral aqueous organic redox flow battery; selective ion-transport; high-permeability; (ferrocenylmethyl)trimethylammonium chloride; methyl viologen

5:00pm **AA2-MoA-15 TiO_2 ALD Thin Films Characterization for SiC Capacitor***, R. César, **José Diniz**,* University of Campinas - UNICAMP, Brazil

Silicon carbide (SiC) has become a very promising material in the microelectronics industry due to its properties. In this way, being widely used in the development of MOSFET, diodes and MOS capacitors, mainly used in high temperature and high power applications. However, the SiC interface presents higher charge density that limits the use of SiO2 as gate dielectric. Dielectric options such as aluminum oxide and titanium oxide (TiO2) have been studied for passivation of interfacial defects. TiO2 stands out due to its qualities such as: high dielectric constant, chemically and thermally stable. Thus, this work presents the study carried out with thin films (15, 25 and 35 nm) of TiO2 deposited by ALD to be used as gate dielectric in SiC capacitors. The structural characterization consists of ellipsometry and spectroscopy Raman. The electrical characterization was performed using capacitance by voltage (CxV) and current by voltage (IxV) using silicon MOS capacitors. Through the ellipsometry technique it was possible to obtain the refractive index (η) values of the TiO2 films, which ranged from 2.06 ~ 2.32. The refractive index of the stoichiometric TiO2 is 2.41. This result indicates that these films have a higher concentration of oxygen than titanium. Raman spectroscopy showed that all films have a rutile crystalline structure, identified by the letter R in Figure 1 (Appendix), and the presence of the anatase crystal structure, identified by the letter A in Figure 1 (Appendix). From CxV and IxV curve, it was possible to it was possible to extract the data that compose the 1, 2 and 3 tables (Appendix). It can be seen from all tables that the VFB values are decreasing in all three cases, indicating the relationship of VFB with the device geometry. Another very important parameter presented by the three thicknesses is the absence of hysteresis. It is very common for TiO2 films deposited by ALD to present hysteresis values greater than 10 mV. Hysteresis is related to charge trapped at the dielectric/semiconductor interface, generated during the device manufacturing process. Therefore, it can be assumed that the capacitors developed in this work have low trapped load values. The 25 and 35 nm thick oxide capacitors presented dielectric constant values with a decreasing behavior, and 15 nm thick oxide capacitor showed an ascending behavior. However, the films showed dielectric constant values ranging from 11 ~ 56. Thus, it can be concluded that these TiO2 films deposited by ALD have rutile and anatase crystal structure, high dielectric constant and low charge density and leakage current density values, being ideal for use in SiC capacitors.

5:15pm **AA2-MoA-16 ALD Can Enable Competitive, U.S.-Sourced Graphite Production***, **Arrelaine Dameron**, D. Higgs, B. Hughes,* Forge Nano

U.S. demand for LIBs is projected to grow to >400GWh by 2030 but U.S. battery manufacturing is currently dependent on foreign (primarily China) supply of graphite materials. The coated spherical purified graphite (CSPG) production processes are energy intensive and derived from petroleum. The spherical graphite is purified by leaching, caustic and thermal treatments to remove metal impurities and is then coated by a liquid phase tar (derived from petroleum processing) that fills surface pores and reduces the surface area. The tar itself is also fractionated and purified through size separation and solvent extraction to produce the ideal precursor feedstock. The coated particles are then dried and baked at >1200 °C for days in an inert-gas oven.

FN has developed ALD coatings to disrupt the pitch coating process. FN has previously shown ALD coatings can improve CSPG graphite. Recently, FN has <u>also</u> demonstrated that ALD can improve uncoated graphite to a higher performance (capacity and rate tolerance) and longer lifetime than pitch

coated graphite with all the added advantages of economically and environmentally improved process to generate a competitive domestic supply of battery grade graphite. This process is applied to the purified and spheronized graphite and then can be directly packaged or cast into anode materials. Drying, thermal treatment and further physical processing are not required. This low vacuum or atmospheric pressure process can we applied continuously at low temperature (<150 °C instead of 1200 °C) greatly increasing the throughput of the process while decreasing the carbon footprint significantly. This nano-coating process can replace traditional tar pitch coating processes for spherical graphite used in the anode of LIB. Combining up incoming US manufacture of high purity graphite and FN's nano-coatings will enable domestic production of low-cost anode-grade graphite materials for lithium-ion batteries and simplify supply chain logistics, while reducing national security risk. Establishing a completely U.S. battery supply chain, using disruptive U.S.-based technology, will deliver both material supply resilience and improved production rates. Use of ALD-coated spherical graphite will also deliver a lower cost and safer battery for U.S. consumption. ALD-coated spherical graphite is a drop-in replacement for foreign sourced materials and seamlessly integrated into standard Lithium-ion battery production methods. This talk will demonstrate the various benefits of ALD coatings on graphite for LIB, scaling these processes to production scale, and compare ALD graphite relative to the incumbent CSPG technology.

5:30pm **AA2-MoA-17 Plasma-Enhanced Atomic Layer Deposition of Nickel and Cobalt Phosphate for Lithium Ion Batteries**, ***Lowie Henderick**, R. Blomme, J. Keukelier, M. Minjauw,* Ghent University, Belgium; *J. Meersschaut,* IMEC, Belgium; *J. Dendooven,* Ghent University, Belgium; *P. Vereecken,* IMEC, Belgium; *C. Detavernier,* Ghent University, Belgium

Since the introduction of a lithium iron phosphate electrode in Li-ion batteries (LIB's), metal phosphates have become increasingly important. Apart from LIB's, metal phosphates have also been proven promising towards e.g. electrocatalytic water splitting, biocompatible coatings, etc., which is why research on their deposition also becomes increasingly important. Atomic Layer Deposition (ALD) has emerged as a deposition technique with unique nanotailoring capabilities, making the combination of both research fields gain a lot of interest. Although it has been challenging to find a suitable phosphate precursor, the use of trimethyl phosphate (TMP) has allowed for the deposition of a variety of metal phosphates (Henderick et al. (2022) *Appl. Phys. Rev.*). Unfortunately, its poor reactivity limits the deposition of metal phosphates with e.g. a high phosphorus-to-metal (P/M) ratio. Interestingly, the use of a TMP plasma (PE-ALD) allowed for the deposition of other, more connected (more P-O-P bonds, figure 1), metal phosphates.

In this work, a novel PE-ALD process was developed for the deposition of nickel phosphate ($NiPO_x$), which was not yet available through ALD. The process is based on an earlier report where a TMP plasma (TMP*) is combined with an oxygen plasma (O_2*) and a metal precursor. Using nickelocene as the metal precursor, saturated growth of an amorphous $NiPO_x$ was observed at a substrate temperature of 300°C, with a growth per cycle of 0.2 nm/cycle (figure 2). Using XPS, the nickel is thought to be in the 2+ oxidation state, while the position of the oxygen and phosphorus peak agree with the formation of a phosphate-like material.

As $NiPO_x$ is currently of interest as a LIB electrode, the material was also electrochemically characterised together with cobalt phosphate using a previously reported ALD process (Rongé et al. (2019) *Nanoscale Adv.*). Both materials showed electrochemical activity (figure 3), although at a lower voltage window than what is supposed to be achievable with these phosphates. This relatively low operating voltage is expected to originate from the 2+ oxidation state of nickel (and cobalt) in the as-deposited material, while a 3+ oxidation state would be needed for the high energy redox reactions to take place. Both materials did show a good rate performance with a reasonable cycle life.

We hope that the novel PE-ALD process developed in this work can help to extent the knowledge on ALD of metal phosphates. We also hope that it sparks interest towards further fine-tuning such processes to optimise the layers towards their respective application (e.g. LIB's and/or other potential applications).

ALD Applications
Room Auditorium - Session AA1-TuM2
ALD for Medical Applications

Moderators: Mato Knez, CIC nanoGUNE, Angel Yanguas-Gil, Argonne National Lab

10:45am **AA1-TuM2-1 Plasma-assisted ALD of IrO_2 for Neuroelectronic Applications**, ***Valerio Di Palma***, *A. Pianalto,* University of Milano Bicocca, Department of Materials Science, Italy; *M. Perego, G. Tallarida,* CNR-IMM, Unit of Agrate Brianza, Italy; *M. Fanciulli,* University of Milano Bicocca, Department of Materials Science. CNR-IMM, Unit of Agrate Brianza, Italy

Investigation *in-vitro* of neural networks is fundamental for the development of strategies to study neurological diseases such as Alzheimer's. Large arrays of microelectrodes (MEAs), planar or micro/nanostructured, are commonly used to stimulate neurons and record their response to external stimuli. MEAs materials are selected to perform charge transfer towards the cells medium efficiently and in a reversible way. IrO_2 has attracted attention in the field because of its pseudo-capacitive behavior, along with its stability and non-toxicity. In parallel atomic layer deposition (ALD) is confirmed as an efficient tool for the conformal functionalization of micro/nanostructured MEAs, with a good control of the thickness and of the physical properties of the film. In this work we report on the ALD growth of IrO_2 thin films and their physical/chemical characterization. The functional properties relevant for neuroelectronic applications, have been addressed with electrochemical measurements. We propose a new plasma-assisted ALD process, using (EtCp)Ir(CHD) as precursor and a mix of Ar/O_2 plasma as reactant. The process exhibits a linear growth, with a growth per cycle of about 0.3 Å at 150°C. *In-situ* spectroscopic ellipsometry shows the typical step-like behavior, *i.e.* the thickness increases during precursor absorption and then it decreases, because of the ligands removal, during the O_2 plasma step.

XRD analysis exhibits the characteristic peaks reported in the literature for the rutile phase of IrO_2. Furthermore, XPS confirms the presence of Ir in the oxidation state of +4, characterized by the chemical shift of the Ir $4f_{7/2}$ component to 61.7 ± 0.1 eV. AFM characterization shows that ALD prepared IrO_2 is smooth and conformal to the substrate. On smooth Al_2O_3 substrates, IrO_2 RMS roughness is 0.7 ± 0.3 nm for a 24 nm thick layer. The chemical characterization via TOF-SIMS indicates that carbon content in the film is below the detection limit, indicating the good quality of the ALD prepared IrO_2.

Electrochemical characterization of the IrO_2/electrolyte interface was performed by impedance spectroscopy (EIS), cyclic voltammetry (CV) and voltage transient (VT) measurements, using a phosphate buffer solution (PBS) as electrolyte. The EIS results indicate that the interaction IrO_2/PBS is purely capacitive, with no faradaic contribution involved in the charge transfer mechanism. In addition, CV measurements confirm that the faradaic contribution is negligible within the range from -0.8 to +0.8 V vs. Ag/AgCl. The charge injection capacity for ALD prepared IrO_2 thin films determined by VT measurements is 1.40 mC, in line with the literature.

11:00am **AA1-TuM2-2 Hydrophilic Surface Modification of Microfluidic Channel by Room Temperature PEALD SiO_2**, ***Chien-Wei Chen,*** Taiwan Instrument Research Institute, NARLabs, Taiwan; *Y. Yu, B. Li,* National Yang Ming Chiao Tung University, Taiwan

Microfluidic devices are often used in biomedical applications for fluidic sample testing and analysis, where multiple tests need to be performed with a small amount of retrieval, and the surface wetness of the flow channel affects the operability and flow rate during sample injection, making it difficult to successfully complete the process with limited retrieval conditions. PMMA is one of the commonly used substrate materials for microfluidic devices, but its surface is relatively hydrophobic (water contact angle >60°), which may be unfavorable when performing aqueous sample analysis.

The most common way to increase hydrophilicity is O_2 plasma treatment, but the short duration and limited increase in hydrophilicity are the biggest inconveniences in use. There are other hydrophilic coating methods such as sol-gel, PVD and CVD, but some of the above process may have the limitation that the process temperature is too high for plastic substrates. On the other hand, these methods require the inner side of the channel to be coated with a hydrophilic layer before it can be assembled into a microfluidic device, which not only increases the complexity of the process, but also may reduce the reliability of the device. For the above reasons, we use room temperature PEALD SiO_2 process to modify the microfluidic surface. ALD SiO_2 thin film not only has better and longer hydrophilic properties than O_2 plasma treatment (Figure 1), but also takes advantage of the fact that ALD can be used to deposit a uniform cover film on non-planar or high aspect ratio structures, and can directly deposit SiO_2 hydrophilic film on the internal surface of the assembled microfluidic channel. The possibility of contamination of the microfluidic surface during assembly is reduced. Finally, we also designed a simple microfluidic device to verify its autonomous absorption of aqueous solution (Figure 2), which can be used to inject fluidic samples without additional pump system and has high potential for Point-of-care testing.

11:15am **AA1-TuM2-3 Atomic Layer Deposition (Ald) on 5-Aminosalicylic Acid for Delayed and Targeted Drug Release Treatment of Inflammatory Bowel Disease**, ***Jaynlynn Sosa,*** University of Central Florida; *P. Banerjee,* University of Central Florida

The incidence of chronic diseases continues to increase worldwide. Exploring new treatment alternatives for chronically ill patients has therefore been an active field of research. To improve patient compliance and reduce harsh side effects, delayed drug release systems have been developed. However, the techniques currently used to coat pharmaceuticals still face limitations in specific site targeting, loading efficiency, and pH tunability when administered orally. To overcome these challenges, we demonstrate the potential of using atomic layer deposition (ALD) as a technique to coat 5-Aminosalicylic acid (5-ASA)—a pharmaceutical drug to treat inflammatory bowel disease—to control the release of 5-ASA throughout the gastrointestinal tract.

5-ASA drug release was investigated by coating 7 mm pellets with 300, 150, and 75 cycles of ALD Al_2O_3. All pellets were made using a hydraulic pellet press and were then coated using an ALD Fiji Veeco® system at a deposition temperature of 120°C to avoid the decomposition of the organic material. To understand the dissolution rate of the coated pellets, we performed kinetic studies using a UV-1800 Shimadzu spectrometer by monitoring the 5-ASA UV signal at 298 nm. Each pellet was analysed for extended periods of time (< 20,000 seconds) in acidic media with various pH's to track dissolution rates. Successful coating on the 5-ASA powders was further characterized by high resolution transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDX).

Through our investigation, we show ALD's potential in coating 5-ASA as a proof-of concept to achieve delayed and controlled drug release that is tunable based on the ALD coating thickness/chemistry. Our research seeks to promote further research and interdisciplinary collaboration between ALD and pharmaceutical researchers to discover new pathways for personalized treatment for patients who suffer from chronic illnesses.

11:30am **AA1-TuM2-4 Atomic Layer Deposition Enables Dimensionless, Biocompatible Encasings for Medical Implants Pro-Longing Their Lifetime**, ***Juhani Taskinen***, *R. Ritasalo, M. Pudas, T. Blomberg, M. Matvejeff,* Picosun Oy, Finland **INVITED**

All kinds of medical devices – various types of implants and wearables - must withstand the corrosive environment of salts, temperature variations, electrical stress, and pollutants, inside and outside the human body, for prolonged periods of time. Hermetic sealing of the device to protect it from the outside environment when used in contact with the human body, (and further to protect the body from the device) is a key step to enable a longer service lifetime, better patient safety, and lower number of replacement surgeries.

To make a robust protective sealing for the medical device, the film properties must fulfill many criteria. First and foremost, the film material needs to be non-toxic for human cells, i.e., biocompatible. Secondly, the film needs to function as an extremely good diffusion barrier against the ions and molecules present in body fluids, while also blocking any leaks (ion or molecular) from the device into the body. In addition, the adhesion of the film to the device surface needs to be high enough that delamination of the film will not occur.

Since Intel introduced ALD HfO2-based high-k into their mass production line in mid-2000's[1], ALD has been a gold standard coating method in various electronics industries, and it is now doing the same in the medical field. A key benefit of an ALD coating is that it is one of the very few ways to make a barrier that leaves no surface of the device "visible" to the surroundings, making the device "invisible" to human body fluids and the immune system. Without an immune response, ALD coated device lasts longer than devices that are coated through other methods. At the same time the ALD coatings are virtually dimensionless, e.g., enabling

miniaturization of all MEMS devices and improving surface activity on orthopedic implants.

The advantages of ALD over other deposition techniques makes it a powerful method for applications where sensitive substrate materials combined with extreme demands on coating quality and temperature / chemical resistance are needed, such as those often seen in the medical applications.

We will present applications and use cases of ALD in the medical field.

Keywords:

Electronics, encasing, biocompatible, medical devices, electronic implants, implants, immunology

Ref. [1] K. Mistry et al., Electron Devices Meeting 2007, IEDM 2007, IEEE International (2007), pp. 247-250.

ALD Applications
Room Van Rysselberghe - Session AA2-TuM2
ALD for FEOL

Moderators: Cheol Seong Hwang, Seoul National University, Jonas Sundqvist, BALD Engineering AB

10:45am **AA2-TuM2-1 High ALD Equipment and Precursor Demand and 5-Year Forecast Due to Continued Semiconductor Device Scaling and Fab Expansions*, Jonas Sundqvist,*** Stockholm, Sweden **INVITED**

The global market for ALD and CVD are experiencing high growth [1]. Total precursor market grew 20% in 2021to approach US$1.4B and will increase by 13% topping US$1.5B in 2022

1. Metal & High-k CAGR (2021 to 2026) = 9.3%
2. Dielectric CAGR (2021 to 2026 = 6.9%

The growth is driven by advanced logic, DRAM and 3DNAND memory chip fabrication needs. In the short-term forecast, sees the global semiconductor market as very healthy with 15-20% YoY growth in 2021 revenues [2], and overall critical materials market growth >7% YoY. All ALD/CVD metal precursors are in healthy demand, since ALD is critical for fabs running 22-45nm nodes as well as for fabs at the leading edge at 16/14 nm and below. In particular, Co and Hf precursors saw high growth in 2020 and 2021 and are forecasted to see strong demand through 2026. Zr used for DRAM capacitors saw a lower growth but is a big segment on its ow. Ru metal is slowly replacing some of the Co and W interconnects on the most advanced logic chips, with anticipated precursor revenue growth to US$10M in 2025 for this highly strategic material. Metals to observe the next years include Mo, Nb and La. Implementation of ALD in emerging new technologies has high potential since all industries are at Giga scale in HVM: PV, Display, MEMS, Power Electronics, LED/µLED, Optical, Lithium Battery, Solid State Fuel Cells, Parts and powder coating and Medical.

ALD materials and OEM tools are needed for multi-patterning lithography used with DUV Immersion and with EUV in leading logic and memory fabs. Multi-patterning typically uses low-temperature PEALD, either in clusters of 8-16 single-wafer chambers, or in “Spatial” high-throughput tools. It is anticipated that fab investments in Asia will allow South Korean and Chinese OEMs to win near-term ALD orders, and they may soon compete with US, EU, and Japanese OEMs in the global tool market for standard processes that are commoditized. Recent actions taken by the new US administration has boosted logic fab investments in the US and several leading-edge fab investments are on the horizon the next three to five years, which will generate a need for both ALD equipment and a healthy precursor supply chain on all materials above going forward.

[1] TECHCET LLC CA, Critical Materials Reports™ 2021

[2] TECHCET LLC CA, 2021 Critical Materials Council (CMC) Conference, Apr. 14-15, San Diego, USA

11:15am **AA2-TuM2-3 High-k Gate Dielectrics for ScAlN Barrier HEMT Structures*, Neeraj Nepal,*** *V. Wheeler,* U.S. Naval Research Laboratory*; . Downey,* U.S. Army Research Laboratory*; . Hardy, D. Meyer,* U.S. Naval Research Laboratory

There has been increased interest in ScAlN-barrier high electron mobility transistors (HEMTs) as ScAlN has larger spontaneous and piezoelectric polarization fields than those in GaN and AlN, which can lead to larger two dimensional electron gas (2DEG) densities. Also, ScAlN with 18% Sc content is nearly latticed matched with GaN and has bandgap of 5.65 eV. Thus, ScAlN can provide a strain-free barrier for GaN HEMT structures with high carrier concentration. Recently, we have demonstrated ScAlN-barrier GaN HEMT structures with electron mobility of 910 cm^2/V-s and 2DEG density >3x10^{13} cm^{-2} [1]. However, these ScAlN/GaN HEMT devices still suffer from high leakage current [2]. Integrating gate dielectrics into these novel ScAlN-barrier HEMTs is necessary to decrease the leakage current, maintain high electric field breakdown and mitigate dc-RF dispersion in order to realize the full potential of these devices.

In this talk we report growth optimization and electrical properties of atomic layer deposition (ALD) grown TiO_2 gate dielectric on ScAlN-barrier HEMTs using Ultratech Fiji Gen2 ALD reactor. ALD process windows were initially monitored and optimized on Si substrates using *in-situ* ellipsometry. Films were deposited using tetrakis(dimethylamino)titanium (TDMAT) and an Ar/O_2 plasma at 300W. The TDMAT precursor temperature was maintained at 75 ^oC, while the pulse duration was varied from 0.25 to 0.35 sec. The plasma gas chemistry was also optimized. Optimal deposition parameters were used as initial condition to further optimize ALD conditions on ScAlN surface. On ScAlN barrier HEMT structures, deposition temperature was varied from 150 to 350 ^oC.

Atomic force microscopy was measured before and after ALD deposition showing minimal change in roughness as a result of the TiO_2 deposition.Contactless resistivity measurements performed before and after ALD and were also consistent, indicating that no plasma induced damage was occurring during ALD gate deposition. Vertical current-voltage and capacitance-voltage measurements were made on a Schottky-contacted HEMT structure and compared to devices with TiO_2 gate dielectrics deposited at different temperatures to discern the full electrical impact. As an example, an extracted dielectric constant of TiO_2 layer deposited at 200°C with O_2 flow of 20 sccm was 50 with no significant change in 2DEG density (changed from 2.7x10^{13} cm^{-2} to 2.6x10^{13} cm^{-2}after TiO_2 layer). Finally, we will present the band alignment of an optimum ALD TiO_2 on ScAlN structure using x-ray photoelectron spectroscopy.

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11:30am **AA2-TuM2-4 Ultra-thin High-κ Dielectrics Growth by ALD on MoS_2*, Emanuela Schilirò,*** *R. Lo Nigro,* CNR-IMM, Italy*; S. Panasci,* CNR-IMM, Department of Physics-University of Catania, Italy*; A. Mio,* CNR-IMM, Italy*; S. Agnello, F. Gelardi,* Department of Physics and Chemistry, University of Palermo, Italy*; F. Roccaforte, F. Giannazzo,* CNR-IMM, Italy

MoS_2 is one of the most investigated 2D-materials belonging to the wide class of transition metal dichalcogenides (TMDs). The great interest in MoS_2 is mainly attributable to the existence of a bandgap that, differently from graphene, makes it suitable also for logic and switching devices. In particular, monolayer-MoS_2 presents a direct-gap semiconducting behavior with a bandgap of 1.8 eV. However, to guarantee high-performance in terms of field-effect mobility (100-500 cm^2/V s), sub-threshold swing (~ 70 mV/dec) and on/off ratio (~ 10^8) the MoS_2-devices requires high-κ dielectrics (Al_2O_3, HfO_2) as top-gate layers. Atomic layer deposition (ALD) is the most appropriate technique to grow uniform high-κ layers with accurate control of thickness. Nevertheless, the uniformity of ALD-nucleation on 2D surfaces can be poor due to lacking out-of-plane bonds, which should act as nucleation sites. Seed-layers and/or pre-functionalization are, hence, necessary to activate ALD-growth on 2D-materials. Their undesired effects on the interfacial quality with 2D-materials encourage the research of new solutions. The substrate, as the driving force of nucleation, is one of the more promising. In fact, similarly to graphene [1,2], also for MoS_2 [3], a metal substrate (gold), has been demonstrated to be a key factor to obtain uniform ultra-thin layers of Al_2O_3. In this work, a large area of monolayer-MoS_2 was exfoliated from bulk molybdenite to a gold substrate. Direct ALD processes of Al_2O_3 and HfO_2 were carried-out on MoS_2/Au substrate, and the structural and insulating properties of high-k were investigated. In particular, ALD coverage degree was evaluated, using standard and conductive-AFM, since the early stage of nucleation. Lower coverage was found for HfO_2, during the early cycles of deposition (40 cycles), than Al_2O_3. However, for longer processes (80 cycles), both high-k show similar ad optimal coverage (higher 95%) but also propitious structural and insulating properties already from very ultra-thin thickness (~ 3.5 nm). Uniform, adherent and compact layers were observed by HR-TEM characterization. Homogeneous insulating

behavior and congruent breakdown electric field values were demonstrated, for both high-k, by conductive-AFM measurements.

These results can have an important impact on the realization of devices based on large-area MoS_2 membranes.

This work has been supported by the FLAG-ERA JTC2019 project “ETMOS”

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[2] E. Schilirò et al Adv. Mater. Interfaces 1900097 (2019).

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11:45am **AA2-TuM2-5 Fabrication of a MOSFET Based on ZnO Using an Atomic Layer 3D-printer***, **Sonja Stefanovic**, N. Gheshlaghi,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; I. Kundrata,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Dominica*; D. Zanders,* Ruhr Universität Bochum, Germany*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Area-selective atomic layer deposition (as-ALD) is bottom-up nanofabrication by using atoms as building blocks. As-ALD has the potential to overcome many of the challenges the semiconductor industry is facing by enabling self-aligned fabrication, instead of lithography’s cost, complexity. However, the main challenges in as-ALD are the need for pre-patterned substrates, defects outside of the desired growing area resulting from insufficient selectivity, and a limited selection of substrate materials that allow deposition.

We have devised and manufactured a direct patterning atomic layer 3D-printer (AL 3D-printer) equipment with a special nozzle design that enables producing direct patterning of various materials with atomic precision. Our invented device is a flexible and efficient tool for reducing the cost and time spent for designing and manufacturing. AL 3D-printer in principle functions similar to conventional g-ALD and all the commercially available precursors which have been used in g-ALD are compatible with our invented equipment. i.e. we have already deposited different materials such as TiO_2, Pt, SiO_2, Al_2O_3 successfully. In addition, the special design of the device allows us to explore new reactions with precursors which are not preferred because of their low vapour pressure or less reactivity.

In this work, we focused on the development of ZnO films with water and a new precursor named $Zn(DMP)_2$(DMP = dimethylaminopropyl) which has a very low vapour pressure compared to a well-studied diethylzinc ($ZnEt_2$) precursor which has a very high vapour pressure and reactivity. Using the proposed direct patterning technique, high-aspect-ratio patterns of ZnO films with our new precursor were fabricated. The patterned films are closed-packed with sharp edges and residual-free surfaces. Our characterization results on the deposited ZnO films with our new precursor shows they have the same structure and composition as with $ZnEt_2$. The produced films are crystalline and the crystals are oriented in a roughly isotropic manner. The growth rate is 1.0 Å per cycle at 200°C. Finally, to assess the reliability and feasibility of the proposed direct patterning method in microelectronic applications, we fabricate a metal oxide transistor MOSFET to demonstrate the practical applications of the device.

ALD Applications
Room Van Rysselberghe - Session AA1-TuA

ALD for Display Applications

Moderators: Jin-Seong Park, Hanyang University, Ganesh Sundaram, Veeco-CNT

1:30pm **AA1-TuA-1 Atomic Layer Deposition for Display from Photoluminescent Materials to Devices and Encapsulation***, **Rong Chen**,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, China **INVITED**

As display plays an increasingly important role, from mobile phones, display screens, to AR/VR and metaverse glasses. There are increasing demands for pursuing more vivid displays, requiring higher resolution, wider color gamut with high stability. Atomic layer deposition (ALD) has been developed as an attractive method to modify and stabilize the photoluminescence materials and devices.[1] In this presentation, several applications through ALD are introduced. For photoluminescence (PL) applications, ALD is performed to coat dense layer on fluoresce materials and passivate defects. For example, Al_2O_3 coating on RLSO:Eu^{2+} phosphor demonstrates outstanding moisture resistance and PL stability.[2] For quantum dots, low-temperature plasma enhanced ALD is developed to enhance the stability of $CsPbBr_3$ QDs films in light, water and heat, which originated from the crystal stabilization after coating.[3-5] Ultra-stable luminescent microspheres structures are fabricated to confine QDs with SiO_2 sphere to improve stability for backlight display.[6] In terms of light-emitting diode (LED), ALD is exploited to infill oxides between QDs, improving the carrier mobility.[7,8] The ultrathin functional layers prepared with ALD could effectively balance the carrier and block the migration of metal ions from the electrode to the functional layers to avoid device damage.[9] For flexible encapsulation, ALD plays an important role for OLED, QLED and micro-LED etc.,[9] inorganic-organic composite layers, nanolaminated packaging structures with total thickness of 100 nm are fabricated as encapsulation layer and significantly improve mechanical stability under bending and stretching tests.[10] The atomic layer infiltration (ALI) has been developed to prepare hybrid organic-inorganic layers with better flexibility.[11,12] Our works provide a versatile method for LED illumination and flexible displays, it is also beneficial to fabricate oxides with high mobility (ZnO, IGZO etc.) for TFT, in the future, the manufacturing equipments (spatial ALD, particle ALD) with mass production capability are also urgent needed for commercial applications.

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[8]*ACS Applied Electronic Materials***2021**, *3*, 2398.

[9]*Advanced Materials Interfaces***2020**, *7*, 2000237.

[10]*Advanced Materials Interfaces***2021**, *8*, 2100872.

[11]*Dalton Trans***2021**, *50*, 16166.

[12]*Advanced Materials Interfaces***2022**, 2101857.

2:00pm **AA1-TuA-3 High-Stability and High-Performance PEALD-IZO/IGZO Top-Gate Thin-Film Transistor via Nano-Scale Thickness Control***, J. Park, **Yoon-Seo Kim**, W. Lee, H. Oh, T. Hong,* Hanyang University, Korea

Oxide semiconductors have already been adopted for mass-production of display backpanes because of their advantages of high field effect mobility (10~30 cm^2/Vs), large-area uniformity, low-cost manufacturing and low-temperature process. The next generation of display technology such as super high vision and memory/logic technology requires the semiconductor which has electron mobility higher than 30 cm^2/Vs with high stability. In addition, for application in 3D structures such as 3D NAND, uniform thickness and composition control in 3D structures are required. Therefore, further than the conventional PVD method, it is necessary to study ALD-based oxide semiconductors that can control the thickness of an atomic level and form a film with low defects based on self-limit reaction. Furthermore, the ALD method facilitates the development of high-performance oxide semiconductors by controlling the homogeneous/heterogeneous vertical structure and composition. Therefore, ALD is suitable as a powerful deposition method candidate for oxide semiconductor development. However, since most research of stacking oxide semiconductor which is the methods to overcome the mobility and reliability trade-off is based on sputter or solution deposition, the ALD-based oxide semiconductor stack studies have rarely been reported. In this study, PEALD-based IZO (back-channel)/IGZO top gate thin film transistor investigated relation between the thickness of the IZO layer and electrical/reliability properties of devices. The mobility increases proportionally according to the IZO thickness. In addition, the PBTS reliability is excellent with an absolute value ΔV_{th} of less than 0.4 V in all of PEALD based TG-TFTs. In particular, the reliability of PBTS is improved proportionally according to the IZO thickness in IZO/IGZO TFT compared to IGZO TFT. Finally, we fabricated PEALD IZO/IGZO TG-TFTs with high mobility (~40 cm^2/Vs) and high stability of PBTS under 10800 s (ΔV_{th} = -0.07 V) through nano scale thickness control.

2:15pm **AA1-TuA-4 Atomic Layer Infiltration Enabled Flexible Encapsulations***, **Fan Yang**, Y. Zhang, D. Wen, K. Cao,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology , China

Due to the, low-cost, large area, light weight, high transparency and high flexibility, polymer based thin-film encapsulation (TFE) and substrates have emerged as one of the most attractive methods for flexible electronics hermetic sealings. However, the intrinsic barrier performances of various polymeric substrates are still too low to prevent moisture and oxygen in an ambient atmosphere to permeate into and degrade the protected devices at its static state, not even mention when at bending or stretching. Different novel configurations, such as wrinkled structures, island-bridge, serpentine structure, origami structure, and helical coil, have been developed to improve the flexibility of polymer FTEs, while at the cost of either low device-coverage density or low transparency. Therefore, effective method and the underlying modification mechanism are in desperate desire for polymer TFEs with high stretchability, excellent transparency, and good barrier property.

In our work, different polymer substrates including polydimethylsiloxane (PDMS) and commercial polyethylene naphthalate (PEN), are modified with atomic layer infiltration (ALI) method. A clear “nucleation-filling-coating” modification mechanism is proposed and elaborated in detail by in-situ quartz crystal microbalance (QCM). The optimized PDMS and PEN hybrid films both exhibit relatively low water vapor transmission rate (WVTR) values and excellent mechanical reliability under bending or stretching conditions. Moreover, patterned sensitive quantum dots (QDs) and based devices encapsulated with the modified hybrid polymer films retain outstanding performances and lifetimes, comparing with ones protected with unmodified polymers. We believe the proposed ALI modification and mechanism will have great and practical implications for encapsulations for future flexible electronics.

References:

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2, Stretchable PDMS Encapsulation via SiO2 Doping and Atomic Layer Infiltration for Flexible Displays. Yinghao Zhang, Di Wen, Mengjia Liu, Yun Li, Yuan Lin, Kun Cao, Fan Yang, and Rong Chen, *Adv. Mater. Interfaces **2021**, 2101857*

2:30pm **AA1-TuA-5 Impacts of Deposition Temperatures on Insulation Properties of Atmospheric Pressure Spatial ALD Al_2O_3 Thin Films for Flexible PEALD IGZO TFT***, **Dong-Gyu Kim**, K. Yoo, S. Lee, W. Lee, J. Park,* Hanyang University, Korea

In the past decades, aluminum oxide (Al_2O_3) has attracted attention because its unique properties such as a wide band gap (~9 eV), a reasonable breakdown electric field (5-10 MV/cm), excellent dielectric properties (6–9), strong adhesion to various materials, and high thermal/chemical stability. There are various Al_2O_3 deposition methods. Among them, atomic layer deposition (ALD) is regarded as a promising conformal film deposition tool. Although ALD-derived Al_2O_3 films have abundant advantages, the ALD method is not always compatible with industrial needs because of its extremely low growth rate (0.1 nm/s). Therefore, many groups have suggested spatially separated ALD (S-ALD) concept to increase growth rate for mass production. In the S-ALD operation, both precursor and reactant are continuously injected and

purged from different zones. A moving substrate crosses each zone for chemical reactions between the adsorbed precursor and reactant, and the time-consuming purge steps are no longer needed. Meanwhile, as market demand increases for flexible display, several researchers developed the S-ALD method that works at atmospheric pressure (AP S-ALD). These include roll-to-roll/sheet-to-sheet processes and low investment costs. Although the AP S-ALD have gained increasing interest, the AP S-ALD-derived Al_2O_3 film properties have not clearly observed as a function of deposition temperatures to date. Furthermore, the possible applications of the oxide-based thin film transistors (TFTs) as an insulator should be evaluated.

In this work, we report AP S-ALD-derived Al_2O_3 growth behaviors with different process parameters. For more in-depth growth temperature studies, we conducted X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) analyses. We fabricated metal-insulator-metal (MIM) devices to evaluate the dielectric constant and breakdown electric field. Based upon results, we used the optimal Al_2O_3 as a B.L and G.I to investigate the application in PEALD IGZO TFT. We evaluated instability of the IGZO TFT as a function of gate field stress time and mechanical bending cycle number to understand the Al_2O_3-adopted PEALD-IGZO TFT flexible display.

2:45pm **AA1-TuA-6 Enhanced Crystallinity Using in-Situ Atomic Layer Deposition Process of Al_2O_3 on P-Type SnO Thin Film and the Associated Device Applications***, **Hye-Mi Kim**, S. Choi, J. Park,* Hanyang University, Korea

Tin monoxide (SnO) is promising p-type material which have low formation energy of tin vacancy (V_{Sn}) and high hole mobility arise from the delocalization of hole conduction path. However, low thermal stability of p-type SnO and facile phase transition to n-type tin dioxide (SnO_2) is major hardship to achieve superior electrical properties and stability[1,2]. In this study, we focused on the effect of Al_2O_3 on SnO film properties especially on the crystal structure and electrical performance. Al_2O_3 is already known for effective materials for the passivation layer of SnO TFT in many reports. However, we figured out that Al_2O_{-3} not only passivate the surface defect of SnO but also highly influence on the crystallinity and following electrical properties. Also, this effect is enhanced when Al_2O_3 is deposited as in-situ ALD process. To identify the mechanism of the improvement of crystallinity, the nucleation energy and the chemical potential difference of SnO and Al_2O_3 stacked SnO crystallites is calculated. SnO TFT with in-situ processed Al_2O_3 exhibits 1.14 cm^2/Vs of field-effect mobility, 4.4E+05 of on/off ratio and low subthreshold swing as 0.15 V/decade. Our study confirms that the mechanism of the improvement in electrical performance of SnO TFT when Al_2O_3 passivation layer is adopted, and in-situ process is far more effective to achieve high performance.

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3:00pm **AA1-TuA-7 Oxidant- and Temperature-Dependent Growth Behavior of ALD-Processed ZnO Thin Films and their Applications inTransistors***, J. Yang, A. Bahrami, **Sebastian Lehmann**, S. He, N. Kornelius,* Leibniz Institute for Solid State and Materials Research, Germany

ZnO thin films were deposited by atomic layer deposition (ALD) using diethylzinc (DEZ) as the Zn source and H_2O and H_2O_2 as oxygen sources. The oxidant- and temperature-dependent electrical properties and growth characteristicsare systematically investigated. Materials analysis results suggest that H_2O_2 provides an oxygen-rich environment so that the oxygen vacancies (V_O) is suppressed, implying a lower carrier concentration and a higher resistivity. The lower growth rate makes it possible for the ZnO thin films to grow along the lower surface energy direction of <002>, leading to a lower Hall mobility. Furthermore, the ZnO semiconductor was integrated into thin film transistor (TFT) devices, and the electrical properties are analyzed. The TFT with H_2O_2-ZnO grown at 150 °C shows good electrical properties, such as a high field-effect mobility of 10.7 $cm^2 V^{-1} s^{-1}$, a high ratio I_{on}/I_{off} of $2{\times}10^7$, a sharp subthreshold swing (*SS*) of 0.25 V $dec.^{-1}$, and a low trapping state (N_{trap}) of $2.77{\times}10^{12}$ $eV^{-1} cm^{-2}$, which provides a new pathway to optimize the performance of metal-oxide electronics.

3:15pm **AA1-TuA-8 Origins of High Off-current of P-type SnO TFTs and Reduction by Source/drain Modulation***, **Su-Hwan Choi**, H. Kim, J. Park,* Hanyang University, Korea (Republic of)

Tin monoxide (SnO) is a promising material for p-type thin-film transistors (TFTs) due to its high hole mobility because SnO forms a delocalized and isotropic hole conduction path with hybridized spherical Sn 5s orbitals and O 2p orbital. However, SnO TFTs have a high off-current because of their ambipolar characteristics, which operate n-type mode at back-channel. The high off-current is undesirable for low power consumption and high CMOS gain. High off current originates from a redox reaction [1], oxygen vacancy generation of SnO [2], and electron injection through source/drain [3] In this study, the origin of the high off-current for P-type SnO thin-film transistor (TFT) is examined by source/drain (S/D) electrode materials. The electrical properties of Ni electrode TFT are superior to the ITO electrode TFT in terms of mobility. However, Ni electrode TFT has a high off-current originating from redox reaction and electron injection through Ni electrode. The ITO interfacial layers (ILs) are adopted to reduce the off-current by restraining the redox reaction and electron injection. For 10nm ITO ILs TFT, optimum electrical properties are achieved, such as field-effect mobility of 2.5 cm2/Vs, a threshold voltage of -1.9 V, a subthreshold swing of 0.43 V/decade, and especially high Ion/Ioff of 1.7×103. Reference : [1] H. Luo, L. Y. Liang, H. T. Cao, Z. M. Liu, and F. Zhuge, “Structural, Chemical, Optical, and Electrical Evolution of SnO,” 2012. [2] J. M. Chem, J. P. Allen, D. O. Scanlon, F. J. Piper, and G. W. Watson, “Journal of Materials Chemistry C,” pp. 8194–8208, 2013, doi: 10.1039/c3tc31863j. [3] L. Y. Liang, H. T. Cao, B. Chen, Z. M. Liu, F. Zhuge, and H. Luo, “Ambipolar inverters using SnO thin-film transistors with balanced electron and hole mobilities,” vol. 263502, pp. 1–5, 2012.

ALD Applications
Room Van Rysselberghe - Session AA2-TuA
ALD for BEOL

Moderators: Scott Clendenning, Intel Corporation, John Conley, Oregon State University

4:00pm **AA2-TuA-11 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Titanium Nitride Using Ammonia Reactive Background Gas***, **Zachary Sobell**, S. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiN_x films. In addition, a new method of EE-ALD was employed with a reactive background gas (RBG) concurrently present during the EE-ALD process (shown in Figure 1). Using the RBG is possible because the hollow cathode plasma electron source (HC-PES) employed for this EE-ALD can operate with reactor pressures in the mTorr range. EE-ALD with a RBG displayed rapid film nucleation and produced continuous, low resistivity ultrathin films. The use of the RBG opens many potential routes for novel EE-ALD film deposition. For example, these ultrathin EE-ALD films should be useful for barriers in backend interconnects.

The TiN_x EE-ALD was performed using tetrakis(dimethylamido) titanium (TDMAT) as the Ti precursor. The EE-ALD was performed using sequential exposures of TDMAT and electrons. During these sequential exposures, ammonia (NH_3) was present continuously in the reactor as the RBG at ~1 mTorr. NH_3 is believed to interact with the electron beam and liberate H and N radicals. The N radicals may facilitate Ti nitridation and the H radicals may remove C as CH_4. Using a RBG was not possible during earlier EE-ALD work with an electron gun because the electron gun has a hot filament that would react with the RBG.

The TiN_x EE-ALD films were grown with the RBG at low temperatures of T<70 °C. In situ ellipsometry demonstrated that the TiN_x EE-ALD films nucleated rapidly on both Si native oxide films (shown in Figure 2) and Si_3N_4 films. The TiN_x EE-ALD films produced using the NH_3 RBG also displayed excellent properties. The composition of the TiN_x EE-ALD films using the NH_3 RBG was close to 1:1 Ti:N as measured by XPS. The carbon content in the TiN_x EE-ALD films was ~2 at.% by ex situ XPS. In contrast, the carbon content was ~60 at.% without the NH_3 RBG. The as-deposited TiN_x EE-ALD films also displayed ultralow resistivities. In situ ellipsometry measured resistivities as low as 105 μΩ-cm (shown in Figure 2). Ex situ spectroscopic ellipsometry obtained resistivities as low as 115 μΩ-cm using a model that agrees well with literature values for the optical properties of TiN. Ex situ four-point probe also measured resistivities as low as 123 μΩ-cm. The TiN_x EE-ALD films were crystalline as determined by GI-XRD. XRR modeling also revealed that the films were dense at approximately 98% of the theoretical bulk density of 5.24 g/cm^3 for TiN.

4:15pm **AA2-TuA-12 Atomic Layer Deposition of MoNx Thin Film Using New Synthesized Liquid Mo Precursor***, **Byunguk Kim**, T. Kang, S. Kim, H. Jeon,* Hanyang University, Korea

Recently, as the resistivity of the metal thin film is increased due to the scaling down of the memory device,interest in Mo metal, which is a metal with low resistivity, is increasing. However, nucleation delay occurs during the deposition process due to the nature of the metal film such as Mo film.To prevent this, the need for a low-resistivity seed layer is emerging. Among them, MoNx film is spotlighted as a seed layer. Because MoNx thin film has excellent thermal stability, low resistivity, and excellent process efficiency because it uses the same precursor as Mo film.

3D-NAND, which is spotlighted as a next-generation memory device, is a high aspect-ratio device, and since a thin film must be deposited with high uniformity on the upper and lower layers, the need for the ALD process is emerging. This is because the ALD process is easy to control thickness and has excellent step characteristics. Therefore, an experiment was performed to deposit a low-resistivity MoNx film using the ALD process. Also, recently, a halide solid precursor such as MoO2Cl2 is used to deposit Mo/MoNx film. However, in the case of a solid precursor, it is difficult to maintain process conditions. Therefore, in this study, a self-synthesized liquid Mo precursor was used to deposit the MoNx film. As reactants, NH3 gas and H2 gas were used. The reason that H2 gas as well as NH3 gas is used as a reactant is that a MoNx film with less impurities can be deposited by reacting with NH3 gas after removing the ligand using H2 gas. XRR, AES, XRD and 4-point probe were used to evaluate the physical and electrical properties of the deposited MoNx film.

As a result of AES analysis of the MoNx film deposited using the ALD process, Mo and N were 62-64% and 29-32%, respectively, and the impurity, C, was detected to be less than 2% and O was detected to be about 5-6%. Additionally, the sheet resistance of the deposited MoNx film was confirmed to be 400ohm/□ confirming that it was a low-resistivity film.

Through the results of this study, it is possible to establish the MoNx film deposition process, which is considered as a next-generation metal seed layer, and we think that the results of this study will be widely used in the next-generation memory device industry.

4:30pm **AA2-TuA-13 Atomic Layer Deposition of Tungsten Nitride Thin Film using WCl_5 as a Fluorine-free W Precursor and its Application into the Diffusion Barrier for Cu and Ru Interconnects***, **Kang-Min Seo**, G. Bea, S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Tungsten(W) is applied to the current semiconductor devices such as W-plug process, metal gate of 3D NAND flash, or bit line of DRAM, due to its extremely low bulk resistivity. Additionally, some thin films of other tungsten compounds like WN_x, WC_x, and WN_xC_y also have an important role in the current semiconductor devices applications as a diffusion barrier. On the other hand, as the size of semiconductor devices has become extremely narrow (in few nm), it has become difficult to deposit a thin film with a precise thickness in a complex structure. In this regard, atomic layer deposition (ALD) seems to be the best option to prepare any thin film which would find its suitability in future technology. So far, the ALD of W or W-based thin films are deposited using WF_6 as a precursor. However, due to the highly corrosive and toxic properties of the F and by-products such as HF, WF_6 thin film process has obvious limitations. In this study, ALD processes using tungsten pentachloride (WCl_5) as an F-free W precursor and various reactants such as NH_3, TBH (tert-butyl hydrazine) molecules, and its plasma as reactants were reported. Preliminary results indicated that, among these reactants, the best quality ALD-WN_x film can be obtained using N_2 + H_2 mixture plasma as a reactant, and further experiments were done mainly using N_2 + H_2 mixture plasma. The deposition was done with a temperature ranging from 200 to 300 ℃at the chamber pressure of ~ 1 Torr. Self-limited growth behavior, the key characteristic of the ALD process was first investigated at the deposition temperature of 250 ℃.At the optimized pulsing condition, the saturated growth per cycle (GPC) was ~1.1 Å. The properties of ALD-WN_x with deposition conditions were analyzed using various tools such as XRD, XPS, 4-point probe, SEM, SIMS, RBS, TOF-ERD, and TEM. The XRD analysis showed that the WN_x thin films have a mix-phase of WN and W_2N. And XRD on WN_x films annealing at high temperature showed a high thermal stability and phase transition (WN to W_2N) at high temperature. Furthermore, the RBS and TOF-ERD analysis showed that the composition of which WN_x thin films has a phase of WN rather than W_2N and reveals relatively low impurities(oxygen, chlorine). Finally, we applied the deposited ALD-WN_x as a diffusion barrier/glue layer for Cu and Ru metallization and the results will be reported in the conference.

4:45pm **AA2-TuA-14 Thermal Atomic Layer Deposition of Ru With H_2 Molecules for Emerging Ru Interconnects***, **Yohei Kotsugi**,* Chemical Materials Development Department, TANAKA Precious Metals, Japan*; Y. Kim, T. Cheon, S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Ru has been in the limelight as one of the alternatives for Cu interconnects due to its shorter electron mean free path than that of Cu. Therefore, in this regard, a lot of Ru-ALD processes have been investigated. However, most of them has been deposited with O_2 as a reactant gas, and there is an inevitable concern that the oxidation of the metallic underlayer may occur even if the Ru film itself is not oxidized. For these reasons, plasma-enhanced ALD technologies have often been proposed, but they also have a problem of the limited conformality on a high AR 3D structure. Here, we introduce plasma-free atomic layered deposition of Ru using H_2 molecule as a non-oxidative reactant and a Ru metal-organic precursor. The film properties, such as the crystallinity, resistivity, impurities contents, and grain size, were compared with those of the film deposited using the same Ru precursor and O_2. The deposition conditions were optimized with regard to the already reported O_2 process. A thin Ru film of ~4 nm was deposited with~100% step coverage on a narrow dual-trench substrate. The low film resistivity of as grown film of ~23.0 μΩ·cm was further reduced to low resistivity of ~10.7 μΩ·cm by the post-annealing (700 °C) treatment. These results suggested that H_2–based thermal ALD process without using plasma-enhanced techniques can also produce high-quality Ru films. However, the resistivity and impurity concentration were slightly higher than those of the O_2 process. Moreover, this H_2-based ALD process has the disadvantage that it takes longer time to complete one cycle than the O_2-based one. In order to overcome the above issues, we designed a new method to minimize the oxidation of under substrates, whereas the film quality was as high as or better than that of the films deposited using O_2 as a reactant. The low resistivity comparable to that of the O_2-based process was obtained in the 40 nm-thick ALD Ru films and it should be noted that, for ultrathin films of 10 nm or less, its resistivity value was even lower than that of O_2–based one. Additionally, the formation of highly pure Ru film with negligible carbon and oxygen impurities were confirmed by secondary ion mass spectroscopy and excellent step coverage on a narrow dual-trench substrate was demonstrated using transmission electron microscopy analysis. The obtained high-quality Ru film can have the potential to be adopted as a Cu substitute material.

5:00pm **AA2-TuA-15 The Oxygen-Free Thermal ALD and Area Selective ALD of Ruthenium Film***, I. Liu,* SAFC HITECH TAIWAN CO., LTD., Taiwan*; **Bhushan Zope**, G. Liu,* EMD Performance Materials Corp.*; J. Woodruff,* EMD Electronics*; J. Chiu,* SAFC HITECH TAIWAN CO., LTD., Taiwan

Ru thin films have been extensively studied for various applications in semiconductor devices such as electrodes for DRAM and MOSFET due to the good stability, low resistivity (7.1 μΩ·cm in the bulk), and high work function (4.7eV). Conventional methods to prepare Ru film are to use plasma-enhanced atomic layer deposition (PEALD) and thermal ALD with oxygen coreactant. As technology nodes continue to shrink, the plasma process may cause poor uniformity and conformality of deposited Ru film. Oxygen coreactant may also result in the oxidation of Ru film or underlying materials. Therefore, oxygen-free thermal Ru processes attract the attention of semiconductor industry to fabricate future devices.

In this study, the newly developed oxygen-free thermal Ru ALD process is reported. Highly uniform, smooth and conformal Ru films were deposited by thermal atomic layer deposition from Ru precursor, RuEM8, and H2 at low deposition temperature (235 ~ 275 ℃). The GPC of RuEM8/H2 process is 0.6Å/cycle. The Ru films grown on SiO2 were smooth (Rq = ~0.22nm) with low resistivity (20 uohm-cm for 8nm film), which indicates good continuity. XPS analysis shows that the Ru films are pure, and the concentration of impurity is under the detection limit. Conformality of Ru growth were studied on via with aspect ratio 20:1. The preliminary results suggest that the conformality can be optimized to 85 ~ 90% (Figure 1).

In addition to basic Ru film growth, area selective ALD (ASALD) applications of RuEM8/H2 process were also studied. For patterning of microelectronics, metal on metal ASALD is becoming an important need to grow metal capping layer or seed layer for gapfill. By incorporating the inhibitor in the process, the RuEM8/H2 can selectively grow Ru film on Ru surface, but not on SiO2 surface. The selectivity of 7.6 (thickness of Ru on Ru / thickness of Ru on SiO2) for RuEM8/H2 ASALD process was achieved (Figure 2)

5:15pm **AA2-TuA-16 ALD-Prepared 2D Transition Metal Dichalcogenides as Diffusion Barriers in Interconnects**, ***Sanne Deijkers***, *A. de Jong,* Eindhoven University of Technology, The Netherlands; *H. Sprey, J. Maes,* ASM Belgium; *E. Kessels, A. Bol, A. Mackus,* Eindhoven University of Technology, The Netherlands

For sub-5 nm technology nodes scaling of interconnects is becoming a real challenge. This holds particularly for Cu diffusion barriers, as the typically used TaN/Ta layers fail at thicknesses below 3 nm [1]. The impossibility to scale the diffusion barrier limits the dimensions of the Cu in the interconnect and thus increases the resistivity drastically. To reduce the thickness of the barrier, the TaN/Ta layers could be replaced by atomically-thin 2D transition metal dichalcogenides (TMDs). In this work we report on the diffusion barrier performance of 2D-TMDs prepared by atomic layer deposition (ALD). Up to this point, literature reports concerning 2D-TMDs as barrier layers are limited to chemical vapor deposition (CVD) processes [2]. The advantages of using ALD are the BEOL-compatible temperatures, the excellent control of both film thickness and morphology, and the high conformality that can be obtained for continuous ultra-thin films on demanding nanostructures.

Various 2D-TMDs have been deposited by ALD at BEOL-compatible temperatures on 90 nm thermal SiO_2. MoS_2 has been deposited using $Mo(NMe_2)_2(N^tBu)_2$ as precursor and H_2S containing plasma as co-reactant [3]. Variations in the process conditions, such as the deposition temperature and the implementation of additional plasma steps, result in different morphologies including amorphous, crystalline and out-of-plane-oriented (OoPO) nanolayers [3]. The barrier performance of the barrier layers against Cu diffusion has been characterized by time-dependent dielectric breakdown (TDDB) tests. Additional insight into the Cu diffusion mechanism through the barrier layer has been obtained from scanning electron microscopy inspection. The results show that polycrystalline MoS_2 displays good barrier performance with a median time-to-failure ($TTF_{50\%}$) of $(8 \pm 1)\cdot 10^3$ s at an electric field of 6 MV/cm. This is a substantial improvement compared to barrierless samples, where $TTF_{50\%} = (1.9 \pm 0.3)\cdot 10^2$ s.

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5:30pm **AA2-TuA-17 Evolution of Structural and Electrical Properties of Molecular Layer Deposited Hafnicone Films after Thermal Processing for Applications in Low-*K* Etch Stops**, ***Vamseedhara Vemuri,*** Lehigh University; *S. King,* Intel, USA; *N. Strandwitz,* Lehigh University

Molecular layer deposition (MLD) yields in conformal hybrid organic-inorganic thin films with precise control over the thickness and conformality similar to atomic layer deposition (ALD). The MLD films have in-organic constituents bonded to organic moieties. This work examines the effect of temperature on the electrical, chemical and structural properties of as-deposited MLD thin films.

The hafnicone films were grown using tetrakis(dimethylamido)hafnium (TDMAH), and ethylene glycol (EG) at 120 ºC. The as-deposited hafnicone films were annealed from 150-350 ºC in an inert atmosphere under a vacuum.

The incorporation of organics and the difference in the chemistry of hafnicone from hafnia films is observed using the ex-situ fourier transform infrared spectroscopy (FTIR). Hafnicone films show a decrease in the intensity of hydrocarbon peaks, whereas the intensity of hydroxyl peaks decreases with annealing in the case of hafnia films. The crystallization behaviour of the hafnia and hafnicone films is probed using the in-situ x-ray diffraction. The ethylene glycol moieties present inside the hafnicone delay the crystallization during annealing when compared to hafnia films. The removal of organics in the hafnicone films may be causing structural collapse and decrease in thickness leading to densification which can be observed by ex-situ X-ray reflectivity data. The dielectric constant of the as-deposited and annealed hafnicone films is lower than as-deposited and annealed hafnia. The dielectric constant of the hafnicone films increases with annealing and can be attributed to removal of organics and densification as observed by FTIR and x-ray reflectivity whereas the dielectric constant of the hafnia films decreases with annealing. This decrease can be attributed to the removal of hydroxyl species after annealing as observed by FTIR. The etch rate of as-deposited hafnicone films is measured in CF_4/O_2 plasma which decreases with increasing annealing temperature to 350 ºC, whereas the etch rate of the hafnia films stays constant even after annealing.

The dielectric constant of hafnicone is much lower than hafnia, and the etch rate of the 350 ºC annealed hafnicone film is similar to the etch rate of hafnia. Our study thus proves that the MLD films offer a high degree of tunability and can be used as potential low-*k* etch stops.

ALD Applications
Room Arteveldeforum & Pedro de Gante - Session AA-TuP
ALD Applications Poster Session

AA-TuP-1 Atomic Layer Deposition of MoS_2 Decorated TiO_2 Nanotubes for Photoelectrochemical Water Splitting, ***Chengxu Shen**, E. Wierzbicka,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*; T. Schultz, R. Wang, N. Koch,* Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*; N. Pinna,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

MoS_2, a prototypical two-dimensional (2D) transition metal dichalcogenide (TMD) material, has been widely applied on multifarious applications such as transistor, catalysis, and energy storage.[1-3] In this work, a low-temperature atomic layer deposition process for MoS_2 thin film is successfully demonstrated by using cycloheptatriene molybdenum tricarbonyl ($C_7H_8Mo(CO)_3$) and H_2S as precursors. The as-deposited MoS_2 films are amorphous while they can be crystalized *in-situ* by sulfurization with H_2S at 300 °C. Moreover, MoS_2/TiO_2 heterostructures are facilely synthesized by depositing MoS_2 onto anodized TiO_2 nanotubes. Photoelectrochemical (PEC) water splitting test have been carried out and our heterostructures exibits a superior PEC performance than pure TiO_2 nanotubes under visible irradiation. This improved PEC performance is attributed to an enhanced light-harvesting ability of MoS_2 and an improved separation of the photo-generated charge carriers. The band structure of the MoS_2/TiO_2 heterostructures is further studied to understand the photoelectrochemical mechanism.

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AA-TuP-2 Impact of ALD-TiO_2 Overlayer on Hematite Nanorod Arrays for the Photoelectrochemical Water Splitting, ***Jiao Wang,*** Humboldt University Berlin, Germany*; L. Liccardo,* Ca' Foscari University of Venice, Italy*; H. Habibimarkani, E. Moretti,* Ca´Foscari University of Venice, Italy*; N. Pinna,* Humboldt University Berlin, Germany

Hematite (α-Fe_2O_3) is an attractive photoanode candidate for solar water splitting because of its favorable bandgap to absorb solar light, nontoxic and abundant. However, the short hole-diffusion length, poor carrier conductivity, and high electron-hole recombination rate especially at surface states significantly limit its practical applications in photoelectrocatalysis. The surface treatment of photoanodes with passivation overlayers have been used to modify the surface states, which can improve the separation and transfer of the photo-generated carriers. Here, hydrothermal grown hematite nanorod arrays were coated with an ultrathin TiO_2 layer by atomic layer deposition for achieving an improved photoelectrochemical performance. Compared to a bare Fe_2O_3 photoanode, the photoelectrochemical water oxidation performance of TiO_2-modified Fe_2O_3 photoanodes is dramatically improved. This improvement is attributed to the surface modification of Fe_2O_3 with the TiO_2 overlayer, which can passivate the surface states, suppress the electron−hole recombination and increase the photogenerated voltage. The effect of TiO_2 overlayer thickness on the overall water splitting efficiency of hematite photoanodes has been systematically investigated. This study demonstrates that a surface treatment with a TiO_2 overlayer is effective and might be extended to other high-performance photoelectrodes for solar water splitting.

AA-TuP-3 Improvement of the Performance of III-IV Multi-Junction Solar Cells Using Atomic Layer Deposited Antireflective Coatings, ***Mantas Drazdys**, D. Astrauskyė, R. Drazdys, T. Paulauskas,* Center for Physical Sciences and Technology, Lithuania

Multi-junction solar cells composed of group III-V semiconductor alloys are widely employed in space and concentrated-sun photovoltaic applications. For the devices to achieve high power conversion efficiency, the reflection losses must be minimized over a wide 400 – 1600 nm spectral range in which they typically operate. Therefore, the design and deposition techniques of antireflection coatings (ARC) play an important role.

The atomic layer deposition (ALD) technique offers several advantageous properties: resulting films are highly conformal, which ensure surface passivation of the structure and protection of the window layer from atmospheric conditions and oxidation. Also, the depositions can be conducted at low temperatures, which prevents unintentional solar cell contact alloying or hardening of photoresist for subsequent device testing. Finally, very high precision thickness control of multilayer ARCs can be achieved, which is a result of self-limiting ALD reactions.

In this work, two different antireflective coatings were deposited on GaAs and AlGaAs subcells and fused silica (FS) glass. The optical design of an ARC typically uses a sequence of layers with high and low refractive indices. For a low refractive index material, Al_2O_3 can be used, since ALD thermal deposition of Al_2O_3 is well known and does not require a complex reactor design. The first ARC was deposited using exclusively thermal ALD and consisted of two layers – TiO_2 and Al_2O_3. To minimize reflection losses over a wide spectral range even further, materials with higher refractive index contrast could be used. Silicon dioxide (SiO_2) is one of the most widely employed materials in the manufacturing of optical coatings owing to its low refractive index and large bandgap. However, it has been shown that the deposition of SiO_2 using a thermal process, where oxidant is water, is not sufficient. Therefore, the second ARC was deposited using a combination of thermal and plasma enhanced ALD and consisted of three layers: Al_2O_3 (thermal), HfO_2 (thermal), and SiO_2 (plasma enhanced).

Here, we present optical coating modelling and deposition results, including reflection spectra, surface morphology, and photovoltaic characteristics comparison of the cells with different coatings.

AA-TuP-4 Li-Nb-O Protection Layer for Li-ion Battery Electrodes *via* Atomic-Layer-Deposition, ***Dae Woong Kim**, W. Hong, J. Park,* Hyundai Motor Company, Korea (Republic of)*; S. Oh,* Hyundai Motor Comp, Korea (Republic of)*; M. Lee, S. Noh, T. Park,* Hanyang University, Korea

Recently, various active materials are being developed as anode/cathode to enhance the performance of next-generation lithium-ion batteries. However, due to the high reactivity occurring at the electrolyte/electrode interfaces, the active material requires a protective layer to improve durability.[1] Unlike general metal-oxide materials, lithium compounds have high ionic conductivity as well as electrochemical stability, so they are considered as one of the ideal solutions for active material protection. Although various technologies are used for coating processes, it is an issue to apply a nano-scale coating to the active material due to thickness control, uniformity, and intrinsic defects of the film. Owing to the attainment of uniform, conformal, ultra-thin, pin-hole free, and thickness controlled deposition of sub-nanoscale films, atomic layer deposition (ALD) is one of the most promising techniques to realize a stable, high-performance thin-film protection layer.

In this work, we have demonstrated Li-ion conductive ALD Li-Nb-O thin films with various compositions were grown by repeated sub-cycle of LiOH and NbOx *via* ALD, and thickness was measured by ellipsometry. The composition of thin films was estimated by XPS and ICP The ionic conductivity of thin films was measured by electrochemical impedance spectroscopy. The experimental results will be presented in detail.

AA-TuP-5 ALD Ge-Se-S Amorphous Chalcogenide Alloys via Post Plasma Sulfurization for OTS Applications, ***Myoungsub Kim**, S. Park, T. Kim, S. Seo, M. Lee, S. Chung, T. Lee, H. Kim,* Yonsei University, Korea

The 3D cross-point memory using chalcogenide amorphous material with ovonic threshold switching (OTS) selector is already required future scaling study for storage class memories and neuromorphic computing systems. The cross-point memory of today`s planar 3D structure is expected to change to a vertical 3D cross-point structure, as in the history of NAND flash, so it is necessary to study chalcogenide ALD for OTS application.[1] We present an ALD study of ternary Ge-Se-S thin films, motivated by the expectation of superior OTS properties over binary Ge-Se and Ge-S, recently published in ALD research.[2,3] Here, we performed DFT calculations and ALD experiments comparing $HGeCl_3$ and $GeCl_4$ precursors based on Se(SiMe3)2 precursors. The ALD $GeSe_2$ thin film with self-limiting behavior is showed to be able to synthesize the novel Ge-Se-S alloys through post-sulfurization process. By changing the temperature and time of the low-temperature plasma sulfurization process, the compositional change of 10 nm-thick $Ge_xSe_yS_z$ thin films were controlled along the $GeSe_2$-Ge_2S pseudo binary line. It was confirmed that the $Ge_5Se_3S_2$ alloys through the two-step process maintained the amorphous phase and excellent step coverage similar to ALD $GeSe_2$. Finally, we compared the OTS electrical characteristics of ALD $GeSe_2$ and $Ge_5Se_3S_2$ amorphous chalcogenide thin films in a mushroom-type device with a 50 nm bottom electrode. The novel $Ge_5Se_3S_2$ exhibited lower off current and superior cyclic endurance up to 1E6 cycles than $GeSe_2$. The achievement of ALD research on novel ternary Ge-Se-S amorphous chalcogenide will contribute to development the future 3D cross-point memory scaling.

Acknowledgments

This paper was result of the research project supported by SK Hynix Inc. We would also like to thank Merck for providing Ge, Se precursors.

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AA-TuP-6 Low-Temperature ALD for Electronic Applications*, Jun Yang, A. Bahrami, S. Mukherjee, S. He, S. Lehmann, K. Nielsch,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science Dresden, Germany

Atomic layer deposition (ALD) is an advanced thin film deposition technique, based on self-limited surface reaction, to dose in the chamber with two or more separated gaseous reactant pulses at a low temperature. The development of semiconductor thin films with good performance may be a true enabler for a variety of applications, such as displays, sensors, photovoltaics, memristors, and electronics. In this poster, a variety of thin films, including ZnO, SbO_x, and Sb_2Te_3 were developed. The quality of the thin film was evaluated using XRD, XPS, and ERDA. Finally, these thin films were successfully integrated on field-effect transistors (FETs) or photodetectors and the performance of devices was discussed.

AA-TuP-7 Atomic Layer Deposition, Annealing and Characterization of FeS_x Layers*, Zsofia Baji, I. Cora, Z. Fogarassy, B. Pécz,* Centre for Energy Research, Hungary

Iron sulphide is an important member of the transition metal chalcogenide group which is presently less researched, although it can be used for a number of different applications. Novel rechargeable batteries, e.g. rechargeable lithium-air (Li-air/O_2) batteries have gained a great deal of attention recently, however, the kinetics of air/O_2 electrodes still pose a problem. Recent research focused on transition metal mono- and di-sulfides, such as FeS as they may be promising electrocatalysts for proton exchange membrane fuel cells, water oxidation, zinc-air battery, and deinsertion/insertion material for Li-ion battery applications.

Transition-metal chalcogenide catalysts have also attracted significant interest recently, due to their activity toward proton reduction to produce molecular hydrogen from water iron sulfide nanoparticles can achieve electrocatalysis for molecular hydrogen evolution with no structural decomposition. FeS can be used as a catalytic material for CO_2 adsorption and the purifying of groundwater and soil.

The atomic layer deposition of iron sulfides promises a number of technological advances, such as precise composition and the possibility to grow few-monolayer thick films and nanostructured layers. However, there is so far only one report on the ALD of FeS using the precursor Bis(N,N'-di-t-butylacetamidinato)iron (II). This work focuses on a further investigation of this deposition process by changing the deposition temperature pulse lengths and by applying different annealing procedures. We examined the composition and structure of the prepared layers by transmission electron microscopy and found that by optimising the deposition parameters, high quality epitaxial FeS films can be grown, moreover, with slight changes in the parameters, the stoichiometry can slightly be influenced, through which the electrical and magnetic properties of the material may be changed.

The layers were deposited in a Picosun Sunale R-200 reactor using Bis(N,N'-di-t-butylacetamidinato)iron (II) and H_2S. The used substrates were sapphire and silicon. The depositions were performed at temperatures between 250 and 450°C. Some layers were treated by post-deposition annealing for an hour performed in the same ALD reactor at 500°C in H_2S atmosphere.

AA-TuP-8 N-Doped TiO_2 Nanotubes Synthesized by Atomic Layer Deposition for the Degradation of Acetaminophen*, Syreina Alsayegh,* Institut Européen des Membranes, France*; M. Bechelany,* Institut Européen des membranes, France*; M. ABID, F. TANOS,* Institut Européen des Membranes, France*; G. LESAGE, F. Zaviska,* Institut Européen des membranes, France

Titanium dioxide is widely used in photocatalysis applications for wastewater treatment due to its benefits. However, its wide band gap and fast electron-holes recombination limits its use under visible light. Many techniques have been used for elaboration and modification of this catalyst. Investigations demonstrated that Titanium dioxide (TiO_2) structure plays a major role on enhancing the degradation efficiency of different micropollutants present in wastewater. Titanium dioxide (TiO_2) nanotubes have attracted much interest in photocatalytic degradation due to their large specific surface area and highly ordered structure. Atomic Layer Deposition (ALD) proves to be very suitable for elaboration of well-structured photocatalysts. In this work, N-doped TiO_2 nanotubes (NTs) were successfully prepared by ALD followed by a thermal treatment for nitrogen doping. The photocatalytic efficiency of these nanotubes was compared to TiO_2 nanofibers (NFs) for the degradation of acetaminophen (ACT). Therefore, the acetaminophen degradation performance on the nitrogen-doped photocatalyst is much enhanced and superior to that of TiO_2 nanofibers prepared by electrospinning. The morphology and structure of these materials were investigated by several characterization techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Photolumiscence measurement were also achieved, and TiO2 NTs shows a lower PL intensity than TiO_2 NFs. The lowest PL intensity correspond to a lower recombination of electron-holes, consequently higher degradation efficiency. The nanotubes were doped with Boron and/or nitrogen in order to enhance its photocatalytic activity for acetaminophen degradation. Among the different doping, nitrogen doped TiO_2 demonstrated the best catalytic properties. The degradation efficiency of N-TiO_2-NTs was 5 times higher than TiO_2-NFs with a degradation rate of 0.05 and 0.01 mg.L-1 .min-1 , respectively. In addition, the photocatalyst has shown a high stability after 4 repetitive cycles, then the stability slightly decreased after the fifth cycle. Acute toxicity assays confirm the release of high toxic sub-products during the first hours of ACT degradation but the toxicity decreased markedly to lower values than initial ACT toxicity after 5 hours irradiation

AA-TuP-9 Iron-Nickel Oxide and Iron-Nickel Sufide Deposited by Atomic Layer Deposition for the Oxygen Evolution Reaction in Alkaline Media*, Estelle Jozwiak,* Humboldt University Berlin, Germany*; N. Pinna,* humboldt University Berlin, Germany

Iron-Nickel alloys in their oxides and sulfides form have already made their proof as electrochemical catalysts for the oxygen evolution reaction. In those alloys both nickel and iron atoms play a different and a complementary role regarding the OER activity: The nickel ones act as active sites while the iron atoms act as an electron relay during the oxygen production. Regarding to the sulfide ions their role is more indirect. They will be exchange by oxide ions during the OER leading to the creation of defaults that will reveal new active sites and so increase the catalytic activity. In this study iron-nickel oxides and sulfides alloys were deposited by atomic layer deposition on carbon nanotubes using nickelocene and ferrocene as metallic sources, and, ozone and hydrogen sulfide as co-reactants. Different ratios of metals were used during the deposition which showed a morphological variation of the final deposited layer. The co-reactants choice also led to a variation of the final morphology. All the samples were tested as catalyst for the OER by using a rotating disc electrode in order to improve the catalysts performance.

AA-TuP-10 Forming-Free Non-Linear Resistive Switching Memory Devices With ALD-Grown HfO_X/TaO_X Bilayers*, Mari Napari, F. Simanjuntak, S. Stathopoulos, T. Prodromakis,* University of Southampton, UK

Resistive switching random access memories (RRAM) have been extensively studied in recent decades because they could potentially be the future of data storage and replace the NAND flash memory when its scaling ends [1]. Several challenges in the RRAM design still remain such as the necessity of electroforming operation to activate the devices with high voltage, and sneak-path issues in the array [2]. Here, we present our work on RRAM devices with HfO_x/TaO_x bilayers grown by thermal and plasma enhanced atomic layer deposition. These devices with ultra-thin switching layer thickness (< 10 nm) are able to perform electroforming-free with non-linear characteristics. The insertion of the HfO_x layer induces the switching behaviour in the single-layer TaOx Zener diode. We also confirmed that this phenomenon persists with both the Pt/Ti and TiN electrodes. We discuss the multi-bit operation of the devices and the factors impacting their stability (retention & endurance), uniformity and scalability. This discussion on the device performances is supported by X-ray photoelectron spectroscopy characterisation of the thin films and their interfaces.

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AA-TuP-11 Film Properties of Al_2O_3 on Si and Graphene substrates deposited by UV Enhanced Atomic Layer Deposition*, Geonwoo Park, J. Shin, D. Go, J. An,*
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Atomic layer deposition (ALD) is a technology that can deposit a very thin, uniform, high-quality and dense film. Due to these advantages, ALD technology is being applied to various energy storage and conversion devices such as fuel cells, capacitors, and batteries. Graphene is one of the well-known 2-D materials consisted of strong carbon bonding, and it shows interesting materials properties, e.g., mechanical flexibility, high carrier mobility and surface to volume ratio, and therefore has been widely adopted in energy storage and conversion devices. However, basal plane of graphene is inert due to the strong sp2 carbon bonding, which can inhibit the facile nucleation ALD layer because ALD process is based on chemical reaction with the surface of the substrate. There have been many attempts to functionalize graphene surface such as oxygen plasma, UV-ozone, thermal oxidation treatments, etc. For instance, plasma treatment is well-known method to functionalization of the graphene, but the high ion energy of plasma can etch the graphene, so the intrinsic properties of graphene can be damaged. On the other hand, UV light energy has the advantage of having a directionality (possibly desirable for selective functionalization), mild energy level (a few eV), and easy controllability.

In this study, we incorporated UV-light source into ALD system, i.e., UV-enhanced ALD, and deposited Al_2O_3 film on silicon and graphene substrates. UV irradiation (10mW/cm^2, 3-4 eV) was conducted with control during the reactant pulse & purge step, and the characteristics of the deposited thin film were analyzed. We show that the film quality of the Al_2O_3 thin film on Si and graphene substrates was changed by UV irradiation during the ALD process. As a result, it was confirmed that, as the UV irradiation time increased, the carbon contamination level of the Al_2O_3 thin film decreased with the density increment on the Si substrate. However, when UV-enhanced ALD was performed on graphene substrates, the film density and uniformity were controlled depending on the UV irradiation time. The uniformity and density of the Al_2O_3 thin film increased when UV was irradiated for up to 5-s, while,in turn, the uniformity of the thin film decreased when the UV irradiation time was exceeded over 5-s. We speculate that UV light promotes neucleation site on the silicon substrate, but adversely affects the neucleation on the graphene substrate. This is because O-H bonds on graphene substrate have smaller bonding energy than that on silicon substrate, which can be more easily removed by UV irradiation energy.

AA-TuP-12 Atomic Layer Deposition of Ruthenium Using a Zero-Valent Precursor*, Ella Rimpila, J. Hamalainen, P. King,*
Picosun Oy, Finland

Ruthenium (Ru) thin films have multiple applications in the microelectronic industry. For example, Ru films can be used as a barrier layer for copper interconnect lines in integrated circuits or as electrode material in dynamic random access memory (DRAM) capacitors, and in the future possibly as interconnect material itself.[1–3]In such applications, conformality and precise thickness control of ALD are advantageous. In some cases, the thickness of the films is required to be in the range of only afew nanometres. Uniformity of the Ru films across the substrates is also essential in industrial applications.

According to literature, numerous Ru precursors have been used in ALD during the last two decades.[4,5] The precursors can be classified based on the oxidation state of Ru, for example. Many of the newer precursors are zero-valent, which means that Ru has the oxidationstate of zero. It appears that zero-valent Ru precursors generally have the benefit of shorter nucleation delays compared to Ru precursors with higher metal valences.[5]

In this work, a Ru ALD process using a zero-valent precursor was examined for a 200mm wafer scale Picosun R-200 Advanced single wafer ALD tool. Several process conditions, such as deposition temperature and precursor pulsing time, were varied. Electrical properties of the obtained Ru films were analysed with a four-point probe (4PP), and thicknesses of selected samples were measured by XRR, and resistivities were then calculated based on the resulting data. Nonuniformity of the films was evaluated by 4PP sheet resistance mapping. Additionally, SEM, XRD, and ToF-ERDA analyses were done.

Ru was deposited both directly on native oxide (thermal SiO_2), and on in-situ grown Al_2O_3, which were compared in terms of film resistivity, uniformity, and estimated nucleation delay. Of these, SiO_2 proved to be a more suitable surface for ALD of Ru using this zero-valent precursor. Nucleation delay of Ru growth on SiO_2 was estimated to be negligible.

Conductive and continuous Ru films were grown at a range of deposition temperatures between 230 and 350 °C. Relatively low resistivities were obtained: for example, the resistivity of a 20 nm thick Ru film grown on SiO_2 was 22 $\mu\Omega$cm. At best, nonuniformities (1σ) of under 5% were achieved. Furthermore, a conductive film with a thickness of 2.4 nm was deposited.

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AA-TuP-13 Wake-Up-Free Metal-Ferroelectric-Metal Capacitor Consisted of $Hf_{0.5}Zr_{0.5}O_2$ and Tin(200) Bottom Electrode*, Dong Hee Han, A. Lee, M. Nam,*
Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)*; T. Moon,* Inorganic Material Lab, Material Research Center, Samsung Advanced Institute of Technology, Korea (Republic of)*; W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

KEYWORDS: Ferroelectric, $Hf_{0.5}Zr_{0.5}O_2$, wake-up, local-epitaxy

Wake-up effect in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) based ferroelectric thin films is reported to be due to the stabilization of the orthorhombic phase following the redistribution of oxygen vacancies present at the interface between the electrode and the ferroelectric layer during electric field cycling. [1] This effect adversely affects device reliability of the metal-ferroelectric-metal (MFM) capacitor. To improve the reliability characteristics of ferroelectric-based memory devices, it is necessary to prevent the wake-up effect.

In this study, the ferroelectric properties of HZO according to the crystallographic orientations of the TiN bottom electrode (BE) were investigated. The wake-up-free was shown in the MFM capacitor in which HZO was grown on TiN(200) BE. To clarify the reason of wake-up-free, the crystalline structure of MFM capacitors which were consisted of TiN(111) and TiN(200) BEs were carefully compared. High resolution transmission electron microscopy revealed that HZO film was epitaxially crystalized on TiN surface. Crystallographic orientation of HZO film on TiN(200) was more favorable to form orthorhombic phase than that on TiN(111) considering effective tensile stress on lattice. Therefore wake-up-free and higher remnant polarization of HZO film on TiN(200) were ascribed to prominent portion of orthorhombic phase in the film. Accordingly, controlling preferred orientation of TiN BE will enable robust the ferroelectric characteristics of HZO based MFM capacitors.

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Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

AA-TuP-14 Investigating the Y-Doped HfO_2 Thin Film for the Metal-Insulator-Metal Capacitor Application Using a Cocktail Precursor*, YoungUk Ryu, H. Seol,*
Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)*; H. Oh, I. Hwang, Y. Park,* SK trichem Co. Ltd., Korea (Republic of)*; W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

In recent years, HfO_2 has been attracting a lot of attention as high dielectric constant material utilized to gate insulator and capacitor dielectric. However, the pristine HfO_2 tends to have a monoclinic phase, which has a relatively lower dielectric constant. To demonstrate the tetragonal phase, employing yttrium (Y) dopant has been reported because the Y allows both tetragonal phase formation and enhancing the crystallinity, simultaneously. [1, 2] The Y-doped HfO_2 thin film exhibited dielectric constant as high as 40, and strong dependency in the Y concentration, indicating that a deposition process for homogeneous dopant distribution in the thin film is required.

In this presentation, the atomic layer deposition (ALD) process using a cocktail precursor with a liquid delivery system (LDS) was investigated for the Y-doped HfO2 thin film deposition with homogeneous Y dopant concentration. Also, the change in the electrical properties of Y-doped HfO_2 according to the Y concentration was confirmed and compared with the

crystal structure. The optimized yttrium concentration where HfO_2 grows into a tetragonal phase was identified, and the fraction with the highest dielectric constant was found. Using this, a metal-insulator-metal capacitor with improved performance was developed by constructing a ZrO_2 / Y-doped HfO_2heterostructure. In this study, we developed ZrO_2 / Y-doped HfO_2 structure with a higher dielectric constant than the $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) structure adopted in the current DRAM structure, which is expected to have high process suitability for the current DRAM fabrication.

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Acknowledgments This work was supported by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

AA-TuP-15 Atomic-layer-deposited Molybdenum Dioxide Thin Films as Promising Electrode Candidates for Application to Next-generation-dynamic-random-access-memory Devices*, **Yewon Kim**, A. Lee, D. Han, S. Moon, T. Youn, M. Lee, W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

In dynamic random-access memory (DRAM) devices, TiO_2 one of promising-high dielectric canstant (*k*) materials has been studied to increase the capacitance density. However, TiO_2 deposited by atomic layer deposition (ALD) on TiN whichismainlyusedasanelectrodeinDRAMexhibited an amorphous or anatase phase, which has a low *k* value of less than 40. Meanwhile,by using RuO_2 electrode, TiO_2 can be crystallized into rutile phase, which has higher *k* value of 100, even at as-deposited state by a template effect due to its low lattice mismatch. [1,2] However, RuO_2 electrode have a difficulty applying real devices due to poor thermal stability.

Thus, MoO_2 has been proposed as an alternative oxide electrode for DRAM capacitor.[3] The crystal structure of MoO_2 has similar lattice constant with rutile-TiO_2, resulting in the rutile-TiO_2 formation as does as the RuO_2. Moreover, MoO_2 has an adequate thermal stability even after annealing process. However, developing the MoO_2 deposition process is a challenging issue because the formation energy of MoO_2 is higher than that of MoO_3 throughout the temperature range.

In this study, we used the template effect to develop an atomic layer deposition process for MoO_2 thin films exhibiting high crystallinity and a very high work function. By employing MoO_2, a rutile TiO_2 thin film exhibiting a *k* value as high as 150 was obtained. The high work function was also attributed to leakage current suppression in the metal-insulator-metal capacitor. Eventually, the minimum equivalent oxide thickness of 0.35 nm, the lowest ever reported, was achieved. Therefore, the proposed MoO_2 ALD is applicable to developing next-generation dynamic-random-access-memory devices.

Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

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AA-TuP-16 Improving Properties of Atomic-layer deposited ZrO_2 Thin Film by Employing the Discrete Feeding Method with Various Zr-based Precursors*, **Aejin Lee**, M. Nam, Y. Kim, W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

ZrO_2 is a representative high dielectric constant (*k*) material for dynamic random-access memory (DRAM) capacitors because it has a relatively high dielectric constant (*k*~40) and a sufficient band gap.[1] The conventional atomic layer deposition (ALD), which is well known to be used to deposit ZrO_2 for DRAM capacitors, can secure step coverage and uniformity,[2] but the full saturation required an extremely long feeding time. In addition, the ALD saturated growth rate is affected by a screen effect, in which the physisorbed precursor molecules screen the active adsorption sites for the following precursor.[3] To eliminate the screen effect, the discrete feeding method (DFM) has been investigated. The DFM-ALD was performed by dividing the Zr feeding and purge steps of the conventional-ALD process into shorter several steps (shorter feeding + cut-in purge).[4] The DFM effectively removes the physisorbed precursor through the cut-in purge during precursor feeding and improves the growth rate by 10 %.[5] In addition, since the size of the physisorbed precursor molecules affects the extent to which the active adsorption sites are covered, the effect of DFM differs depending on the size of the precursor molecule.

In this study, the growth behavior and electrical properties of ZrO_2 deposited via ALD with a conventional process and DFM were compared, and the extent to which the precursor size affected the DFM effect was analyzed. Through DFM, it was confirmed that the growth rate of Cyclopentadienyl Tris(dimethylamino) Zirconium (Cp-Zr) and Tetrakis(ethylmethylamino) Zirconium (TEMAZr), which are Zr-based precursors of different size, was increased by 16 and 23 %, respectively. Unlike Cp-Zr, which still has a steric hinderance even when physisorbed precursors are removed by cut-in purge, TEMAZr with a small size has excellent DFM effect by securing enough active sites by cut-in purge. When DFM was applied to both precursors, the crystallinity and density were improved, and in the case of TEMAZr, which had excellent DFM effect, the density was 5.68 g/cm^3, which is the literature value. By securing a high-density thin film, the interfacial properties were also improved.

Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

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AA-TuP-17 Atomic Layer Deposition of AlN Films With and Without Plasma Piezoelectric Effect*, **Noureddine Adjeroud**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Summary

1. Low temperature processes from 180 °C to 250 °C for growing AlN with (002)-preferred orientation by plasma enhanced atomic layer deposition
2. High temperature processes 400 °C to 500 °C for growing AlN with atomic layer deposition
3. Measurement of piezoelectric coefficient $e_{31,f}$ of AlN films: 0.38 C.m^{-2} for 590 nm-thick (002) AlN film

Motivation and results

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 [1]. 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 [2, 3]. 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 (figure 1). In addition, X-ray photoelectric spectrometry surveys (figure 2) confirmed high quality AlN films with low impurities level of 1% of carbon and 6-7% of oxygen, which are comparable to the literatures [4, 5]. The direct piezoelectric coefficient $e_{31,f}$ measurements (4-point bending method, aixACCT), which were rarely reported on AlN films grown by PEALD, revealed a strong correlation between crystallographic orientations and $e_{31,f}$value of AlN films; *i.e.* $e_{31,f}$ coefficient of (100) AlN film was almost "zero", whereas that of (002) preferred orientation film was measured to 0.38 C.m^{-2} (figure 3). 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. Though, AlN film is grown at temperature as low

as 250 °C, the properties of the AlN film 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.

AA-TuP-18 Growth of Rutile TiO_2 on VO_2 by Atomic Layer Deposition for DRAM Capacitor Application, ***Seungwoo Lee***, *D. Han, M. Nam, Y. Kim,* Kyung Hee University, Korea (Republic of)*; D. Kim, K. Kim, Y. Park,* SK Trichem Co. Ltd., Korea (Republic of)*; W. Jeon,* Kyung Hee University, Korea (Republic of)

Among binary transition metal oxides, titanium dioxide (TiO_2) has been widely studied for application to next-generation DRAM capacitor because it has a relatively high dielectric constant (*k*). TiO_2 has different *k* values depending on the crystalline phase. The anatase structure has a *k* value of about 40, and the rutile structure has a higher *k* value of 86 and 170 along the a-and c-axis, respectively.[1, 2] However, rutile TiO_2 is a stable phase at high temperature and requires a subsequent annealing process at very high temperature.[3] Alternatively, it can be formed under epitaxial growth conditions on materials such as RuO_2 which have similar crystal structures to rutile TiO_2.[4] Vanadium dioxide (VO_2) undergoes a reversible phase transition from the low-temperature monoclinic VO_2 to the high-temperature rutile VO_2 at about 67 °C.[5] Rutile VO_2 has less lattice mismatch with rutile TiO_2 than RuO_2.[6] It has also been reported that when TiO_2 was grown on VO_2, oxygen ionic transport to TiO_2 occurred due to the difference in the chemical potential for oxygen between the two materials, which facilitates the crystallization of rutile TiO_2.[7]

Therefore, in this presentation, crystallization of TiO_2 to rutile phase on VO_2 films using the crystal structure similarity between rutile TiO_2 and VO_2 was demonstrated. VO_x film was deposited by atomic layer deposition (ALD) and monoclinic VO_2 was formed using rapid thermal annealing under appropriate O_2 partial pressure. TiO_2 ALD on VO_2 substrates was carried out at a temperature (250 °C) higher than the phase transition temperature of VO_2. The crystalline property of TiO_2 and VO_2 films was investigated by X-ray diffraction. In addition, it was confirmed that TiO_2 grown on VO_2 has a rutile structure by electrical properties analysis.

Acknowledgments This work was supported by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

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AA-TuP-19 Superconducting Nbn: Sputtered Versus Plasma ALD With Bias, ***Tania Hemakumara***, *Y. Shu,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; R. Renzas,* Oxford Instruments Plasma Technology*; V. Gauthier, V. Giglia, S. Nicolay,* Université de Sherbrooke, Canada*; M. Weides,* University of Glasgow, UK*; M. Pioro-Ladrière, D. Drouin,* Université de Sherbrooke, Canada*; R. Sundaram,* Oxford Instruments Plasma Technology, UK

High quality superconducting metal nitrides are crucial for the fabrication of quantum devices. NbN, specifically has been widely used due to its favourable critical temperatures (T_c), where PVD has been the traditional route for the deposition of NbN. However, ALD offers many advantages compared to PVD, including superior reproducibility, composition, and thickness control. For these films to be used in quantum applications, information on film quality and composition are essential. Comparison of sputtered and ALD films enable us to understand how these properties differ and their impact on T_c and crystal orientation. Here we report the potential of ALD with bias based on these studies for various quantum applications. To this end data on electrical, chemical and physical characterisation of the ALD and sputtered films will be provided.

NbN has been deposited using TBTDEN and H_2/Ar plasma at 250ºC using RF substrate bias. Sputtered films were deposited using a pure Nb target and N_2/Ar gas mixture. 50 nm of both sputtered and ALD NbN were deposited on intrinsic Si samples. Sample resistance measurement were performed in a 4-point probe configuration as a function of temperature from 300 K down to 2 K and T_c was extracted by taking the intercept of the slope at the resistance drop point with the temperature axis. In addition, XRD and SIMS analysis were also performed on the ALD film to obtain the crystal orientation and composition of the NbN film.

Sputtered NbN resulted in a T_c of 12 K, this is lower than values stated in literature and is possibly due to the challenging nature of optimizing sputtered nitrides or due to the formation of defects at the Si/NbN interface during the sputtering process. ALD NbN on the other hand has resulted in a $T_c$of 14.5 K. In addition, a (111) crystallographic orientation has been observed on the XRD measurements of the ALD NbN film, which is indicativeof the cubic phase leading to superconductivity. Further, SIMS analysis confirmed low O content on the NbN films proving high quality ALD deposited films.

The enhanced T_c, XRD and SIMS data of ALD NbN with bias is encouraging for the realisation of devices for quantum application.

This work is supported by NSERC Canada and Innovate UK project, “Advanced Manufacturing Toolkit for Quantum Sensing and Quantum Computing”.

AA-TuP-20 Membrane Design by ALD/MLD for Hydrogen Sensing, *S. Sayegh, M. Drobek, A. Julbe,* ***Mikhael Bechelany***, European Institute of Membranes, France

Hydrogen (H_2) is one of the energy vectors essential for the success of the energy transition. In less than twenty-five years, hydrogen is expected to represent 18% of the total energy consumed on the planet thus leading to possible CO_2 emissions reduction by 6 gigatonnes compared to current levels. At the same time, hydrogen energy technologies involve major environmental, research and industrial challenges. In this work, we will address our research implication in the area of hydrogen detection.

The explosive and flammable nature of hydrogen hampers a widespread deployment of this energy vector without an efficient securing production, storage and implementation facilities and equipment, both in industrial or general public sectors. In this respect, hydrogen selective gas sensors are recognized as essential links in this security chain. Depending on the operating conditions, such sensors should fulfill very precise specifications in terms of sensitivity, selectivity, response time, temperature range etc. In our research group, different original approaches in detection and sensor design are currently studied. For instance, gas sensors based on zinc oxide (ZnO) nanowires encapsulated in MOF (Metal Organic Framework)-based molecular sieve membrane have been developed for the selective detection of H_2 in gas mixtures up to 300 °C [1]. Attractively, this concept is applicable to various sensors geometries which could be further functionalized with metal nanoparticles (e.g. palladium)by Atomic Layer Deposition [2] in order to confer the hydrogen sensors with additional sensitivity. The same approach has been applied using ALD of boron nitride as selective membrane for increasing both sensor sensitivity and stability [3]. Moreover and for the sake of enhancing the sensors humidity resistance, Molecular Layer Deposition (MLD) has been recently used to deposit a humidity-resistant nanomembranes on ZnO semiconductor nanowires [4].

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AA-TuP-21 Schottky Diodes to Gallium Nitride Prepared by Plasma-Enhanced Atomic Layer Deposition, ***Suzanne Mohney***, *I. Campbell, A. Molina, A. Agyapong, M. Thomas,* Penn State University

Transition metal nitrides are attractive candidates for Schottky diodes and gate metallizations for group III nitride devices. Many of them are unreactive with gallium nitride and aluminum gallium nitride at elevated temperatures. In addition, some transition metal nitrides are already accepted in typical nanofabrication laboratories, and they can be integrated into processes where dry etching is preferred for patterning. However, transition metal nitride Schottky diodes on gallium nitride reported in the literature are typically prepared by sputter deposition, which can introduce defects in the semiconductor, resulting in high currents under reverse bias and ideality factors much greater than unity. We have fabricated Schottky diodes to n-type gallium nitride by plasma enhanced atomic layer deposition using a remote N_2-H_2 plasma in a Fiji Gen II reactor. Film composition was measured by x-ray photoelectron spectroscopy and energy-dispersive x- ray spectroscopy. When layers with the composition $MoC_{0.3}N_{0.7}$ were prepared

usingbis(tertbutylimino)bis(dimethylamino)molybdenum, diodes to n-GaN had rectifying characteristics as deposited. After they were annealed at 600°C in N_2, the Schottky barrier height increased to 0.87 ± 0.01 eV with an ideality factor of 1.02 ± 0.01. Since the barrier height was measured by the current-voltage technique, the ideality factor will always be slightly greater than unity due to image force lowering of the barrier height. X-ray diffraction and transmission electron microscopy revealed that these films were a single phase, which is beneficial for creating homogeneous diodes. More carbon-rich films with the composition $MoC_{0.8}N_{0.2}$ also displayed rectifying characteristics, but the films contained two phases, the ideality factor of the diodes was higher, and the barrier height was lower. We have also successfully prepared diodes with another precursor (molybdenum carbonyl) and will report the effect of precursor and deposition conditions on the performance of diodes in this presentation. The authors thank ONR for support through N000141812360 (Approved, DCN# 43-9072-22) and A. Allerman (Sandia National Laboratories) for gallium nitride epilayers.

AA-TuP-22 Development of High-k Gate Insulator Deposition Process for Next-Generation Thin Film Transistor Using Atomic Layer Deposition*, **Min Kyeong Nam**, A. Lee, D. Han, S. Lee, W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

Currently, thin film transistor (TFT) based on transparent oxide channel such as amorphous InGaZnO (a-IGZO) has being widely studied as switching devices for liquid crystal displays (LCD) and flexible active matrix organic light emitting diode (AM-OLED) displays.[1] To demonstrate high speed and high resolution display, operation speed and dimension of TFT should be enhanced. In this regard, a gate insulator application of the high dielectric constant (k) materials has been attracted a lot of attentions. Moreover, for deposition of the high-k materials, the atomic layer deposition (ALD) process, which allows relatively low process temperature with adequate thin film quality, is required.

In this study, ALD process of ZrO_2 on IGZO as the gate insulator of TFT was developed using Tetrakis(ethylmethylamino) Zirconium (TEMAZr) and Cyclopentadienyl Tris(dimethylamino) Zirconium (Cp-Zr) as the Zr precursors. The thin film growth behavior and electrical properties of deposited ZrO_2 were strongly affected to the difference in chemistry of TEMAZr and Cp-Zr. The crystallinity of the ZrO_2 film and the formation of an interfacial layer were examined through x-ray diffraction, x-ray reflectometry, and x-ray photoelectron spectroscopy analysis. We demonstrated the possibility of developing a high-performance TFT device capable of low-voltage driving for next-generation displays by evaluating the TFT characteristics of the metal-insulator-semiconductor structure.

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Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea)the BK21 Plus program.

AA-TuP-23 Co-Coated Si X-Ray Optics With Atomic Layer Deposition*, **Yukine Tsuji**, A. Fukushima, D. Ishi, Y. Ezoe, K. Ishikawa, M. Numazawa, T. Uchino, S. Sakuda, A. Inagaki, Y. Ueda, H. Morishita, L. Sekiguchi, T. Murakawa,* Tokyo Metropolitan University, Japan*; K. Mitsuda,* National Astronomical Observatory of Japan

We have been developing an ultra-lightweight Wolter type-I X-ray optic using MEMS technologies for X-ray astronomical observations (Ezoe et al., 2010, Microsys.Tech.2010, 16, 1633) In this paper, we present our first Co atomic layer deposition (ALD) test on a test optic and evaluation of its X-ray reflectivity which is to our knowledge the first demonstration of the Co-coated X-ray optic with ALD.

The MEMS X-ray optic is made of 4-inch Si (111) wafers (300-500-micrometer thickness). The Si wafer is firstly etched to have micropores (20-micrometer width) by deep reactive ion etching, and sidewalls are used as X-ray reflective mirrors. Using high-temperature hydrogen annealing process, we then smooth the sidewalls. With chemical mechanical polishing process burr structures on edges of the sidewalls which block incidence of X-ray are removed. Finally, the wafer is plastic-deformed into a spherical shape to focus parallel X-ray beam from celestial objects. Two wafers deformed to different curvature radii are stacked to form a Wolter type-I optic.

Si is easy to be etched, but its X-ray reflectivity at large reflection angle and high energy becomes significantly lower than those of heavy metals such as Au, Pt and Ir. Therefore, we use ALD to coat heavy metals thin film to the sidewalls of the micropores. We have already demonstrated Ir and Pt film formation (Ogawa, et al., 2013, Applied Optiics, 52, 5949, Ishi, et al., 2020 Applied Express, 13, 087001). For our future space applications (Ezoe et al., 2018， J. Astron. Telescope, Instrum, 4， 046001), we need to increase X-ray reflectivity around 1 keV. We thus tested to form a Co film with ALD, which has excellent reflection characteristics in this energy band.

First, we coated a Co film on the surface of a bare Si wafer as a test. Then, we evaluated the reflectivity of the Co-coated surface at the Al K_α characteristic X-ray (1.49 keV) using the 30 m beamline at JAXA and confirmed a significant improvement in reflectivity at large angles (>1 degrees). Furthermore, the roughness of the Co-coated surface was estimated to be about 1 nm rms by comparison with the theoretical reflectivity. This roughness satisfies the requirement in our future space mission (< 1 nm rms) and can be expected as a candidate for a new film deposition material. Similarly, Cu L_α (0.93 keV) and C K_α (0.28 keV) were also evaluated, and it was found that the surface roughness was 1-2 nm rms, which was close to the required performance. In the near future, we plan to deposit Co film on our micropore optical system and evaluate the performance.

AA-TuP-24 Optimization of High-Performance P-Channel Sno Thin Film Transistor Using Atomic Layer Deposition*, **Myeong Gil Chae**, J. Kim,* Seoul National University of Science and Technology, Korea (Republic of)*; B. Park, T. Chung,* Korea Research Institute of Chemical Technology (KRICT), Korea (Republic of)*; S. Kim,* Korea Institute of Science and Technology (KIST), Korea (Republic of)*; J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

Up to date, oxide semiconductor-based electronics are limited to unipolar devices consisting of n-type oxides owing to the challenges in achieving high-performance p-type oxide counterparts. P-type oxide semiconductors show inferior carrier transport characteristics than n-type oxide owing to localized oxygen orbitals with large hole effective mass at valence band maximum (VBM). Among p-type oxides, SnO regarded as a promising candidate with low defect formation energy of Sn vacancy (V_{Sn}) that produces hole carriers and delocalization of VBM by hybridization of Sn 5s and O 2p orbitals, leading to low hole effective mass and high hole mobility. Meanwhile, atomic layer deposition (ALD) allows precise control of thickness and composition based on self-limiting reaction and layer-by-layer growth by alternately injecting precursor and reactant. Therefore, in this work, we have introduced high quality SnO film as a channel layer of p-type TFT by ALD using $Sn(dmamp)_2$ and H_2O. The strategic probing of key parameters such as the deposition temperature and thickness of ALD SnO film for high performance TFTs resulted in the SnO TFT with field-effect mobility (μ_{FE}) of 6.13–7.24 $cm^2/V\cdot s$ and on/off current-ratio (I_{on}/I_{off}) of 10^4–10^5 without post-annealing processing. Moreover, back-channel passivation with ALD Al_2O_3 film further improved the switching characteristics of the SnO TFT, exhibiting enhanced subthreshold swing (SS) of 3.18 V/dec.

AA-TuP-25 Intense Pulsed Light Annealing of Low-temperature Atomic-layer-deposited SnO Thin Films for P-channel Thin Film Transistor*, **Jina Kim**, M. Chae,* Seoul National University of Science and Technology, Korea (Republic of)*; B. Park, T. Chung,* Korea Research Institute of Chemical Technology (KRICT), Korea (Republic of)*; J. Choi, K. Cho,* Korea institute of industrial technology (KITECH), Korea (Republic of)*; W. Lee,* Myongji University, Korea (Republic of)*; J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

SnO is promising p-type transparent semiconducting oxide known for excellent hole transport property. Its high p-type conductivity is driven by the unique valence band maximum structure composed of Sn 5s–O 2p hybridized orbitals and low formation energy of Sn vacancies generating hole carriers. Especially, atomic layer depositon (ALD) is a suitable process to grow SnO because the oxidation state and film thickness can be finely controlled through the self-limited surface reaction. However, crystalline SnO could be obtained only at >150 ℃ using ALD [1], which would hinder the application of ALD SnO to polymer-based plastic substrates. Therefore, it has been required to develop low-temperature post-crystallization technology to achieve crystallized SnO films without deformation of the flexible substrates. Intense pulsed light (IPL) annealing is considered as useful post-annealing tool with insignificant thermal impact.

Herein, amorphous SnO films were grown by ALD with $Sn(dmamp)_2$ and H_2O as the Sn precursor and reactant at a low temperature of 120 ℃. The IPL annealing was employed to successfully crystallize the SnO films with maintaining oxidation state of Sn^{2+}, resulting in excellent hole transport characteristics. Amorphous SnO film was start to be crystallized at IPL pulse number of 200−300, and the crystallinity was increased with increasing the pulse number. The various properties such as crystallinity, surface morphology, and chemical states of SnO films were characterized by X-ray diffraction (XRD), raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The bottom-gate staggered-structured thin-film transistors (TFTs) were fabricated with Al_2O_3 passivation layer. With SnO films after 200 IPL pulses, remarkable p-type transistor property was achieved with field-effect mobility of 2.49 $cm^2/V{\cdot}sec$, subthreshold swing of 2.85 V/dec, on-off current ratio of $8.2{\times}10^4$.

Acknowledgments This Research has been supported by the KOREA RESEARCH INSTITUTE of CHEMICAL TECHNOLOGY (KRICT) and National R&D Program through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT (NRF-2020M3H4A3082126)

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AA-TuP-26 Hafnium Zirconium Oxide-Based Ferroelectric Field Effect Transistor With Atomic-Layer-Deposited Indium Gallium Tin Oxide Channel Layer*, **Hyeonhui Jo**, J. Won, P. Youn, J. Kim, H. Jang, W. Jo, J. Han,* Department of Materials Science and Engineering, Seoul National University of Science and Technology, Korea (Republic of)

Ferroelectric field effect transistors (FeFET) have received increasing interest as synaptic devices because they can easily imitate the synaptic weights update behavior through analog conductance modulation of the channel layer. In particular, the conductance of the channel layer can be controlled by the multiple polarization states of the ferroelectric layer, which is determined according to the applied gate voltage pulse. Hafniumzirconium oxide (HZO) commonly used in the ferroelectric layer of FeFET has various advantages such as low deposition temperature, ALD capability, and good ferroelectric characteristics despite a thickness of ~10 nm. Also, indium gallium tin oxide (IGTO) is a promising material as the channel layer because it has high mobility despite the amorphous phase and minimizes the formation of the interfacial layer between IGTO and HZO, which induces high operating speed and low power consumption. Moreover, the field effect mobility of IGTO can be improved by increasing In and Sn compositions because both the In-5s and Sn-5s orbitals form the main channel of the electron conduction.

In this work, ferroelectric HZO layer was deposited by ALD at 300 °C using $CpHf(NMe_2)_3$ and $CpZr(NMe_2)_3$ as Hf and Zr precursor, respectively. ALD IGTO channel was deposited at 200 °C using 3-(dimethylamino)propyl]dimethyl-Indium (DADI), dimethyl(N-ethoxy-2,2-dimethylcarboxylicpropanamide)gallium ($Me_2Ga(edpa)$), and tetrakis(dimethylamido)tin (TDMASn). The growth characteristics of ternary HZO and quaternary IGTO films were examined and film properties were analyzed using XPS, XRD, and SEM. FeFET devices were fabricated using HZO and IGTO films as the ferroelectric layer and channel layer and the synaptic characteristics of FeFET devices were investigated by conductance modulation behavior.

Acknowledgments: This research has been performed as a cooperation project of “Basic project(referring to projects performed with the budget directly contributed by the Government to achieve the purposes of establishment of Government-funded research Institutes)” and supported by the KOREA RESEARCH INSTITUTE of CHEMICAL TECHNOLOGY (KRICT) and by National R&D Program through the National Research Foundation of Korea(NRF) funded by Ministry of Science and ICT(NRF-2020M3H4A3082126).

AA-TuP-27 Interface and Electrolyte Design to Enable Stable Zn Metal Anode for Aqueous Zn-ion Batteries*, **Jian Liu**,* University of British Columbia, Canada

Rechargeable aqueous zinc-ion batteries (ZIBs) have attracted increasing attention as energy storage technology for large-scale applications because of low cost, inherent high safety, and high capacity of Zn metal (820 mAh g^{-1} and 5854 Ah L^{-1}). However, the poor rechargeability of Zn anodes limits their development, which is attributed to the dendrite growth, passivation, and hydrogen evolution issues in the zinc anode. This talk will introduce recent progress in addressing these problems associated with zinc anodes by using nanoscale interface engineering and developing novel electrolytes to enable durable and high-performance ZIBs [1]. First, a nanoscale Al_2O_3 coating by atomic layer deposition was applied to modify the zinc-electrolyte interface [2]. The Al_2O_3 coating effectively suppressed the zinc dendrite formation, improved wettability, and inhibited zinc corrosion. As a result, the surface-coated Zn has been verified in Zn-MnO_2 batteries using layered δ-MnO_2 as the cathodes and consequently superior electrochemical performance with a high capacity retention of 89.4% after over 1000 cycles. In the second part, the performance of zinc metal was further improved by using a hybrid organic-inorganic coating (alucone). With the optimal coating thickness (12 nm), an over 11-fold enhancement in the running lifetime (780 *vs.* 70 h) and a reduced overpotential (84.3 *vs.* 110.3 mV) were achieved compared to bare Zn at a current density of 3 mA cm^{-2} [3]. Thirdly, an acetonitrile/water-in-salt (AWIS) hybrid electrolyte was developed and found to prolong the lifespan of Zn|Zn cells from 150 to 2,500 h [3]. More importantly, the AWIS hybrid electrolyte increased the upper cut-off voltage of Zn-MnO_2 batteries from 1.8 to 2.2 V, leading to enhanced energy and power densities. This series of work will provide insights into the design and development of high-performance ZIBs for grid applications.

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AA-TuP-28 ALD-Coated Mesoporous Films for Electrocatalysis*, **Nicola Pinna**, M. Raza,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*; M. Frisch, R. Krähnert,* Department of Chemistry, Technische Universität Berlin, Germany

Water splitting electrocatalysts are in need because of the growing demand for renewable energy and simultaneous depletion of fossil fuels. There are different types of catalytically active oxides used as electrodes for the electrochemical water splitting, both in acidic and alkaline conditions. The catalytic performance of those materials strongly depends on surface composition and morphology. It is possible to increase the catalytic efficiency of such electrodes by increasing the number of active surface sites. Here we report the synthesis of novel electrode with template-controlled mesoporosity and their modification with highly active catalytic species. The improved utilization of active species relies on the synthesis of soft-templated metal oxide supports, and a subsequent well-controlled and conformal modification *via* atomic layer deposition (ALD). The composition, morphology, and crystallinity of the deposited film were controlled by varying different deposition parameters. The structural and morphological properties, as well as the mass activity and stability in the electrocatalytic oxygen evolution reaction were investigated in the order to propose clear structure-properties correlations.

AA-TuP-29 Nanoscale Energy Transport Processes in Chalcogenide-Based Phase Change Materials*, **Kiumars Aryana**, P. Hopkins,* University of Virginia

Modern computing relies on the processing of information by constantly shuttling the data back and forth between the storage and the processing units1. This computing architecture, known as von Neumann, leads to huge traffic jams between the memory and processor, incurring considerable costs in terms of latency and energy. Phase change memory (PCM) is a rapidly growing technology that not only offers advancements in storage-class memories but also enables in-memory data processing to overcome the von Neumann bottleneck. In PCMs, data storage is driven by thermal excitation. However, there is limited research regarding PCM thermal properties at length scales close to the memory cell dimensions. Our work uses the knowledge of carrier dynamics to experimentally identify an optimal thickness for the phase change material based on a balance of thermal conductivity and crystallographic-phase-dependent interfacial thermal resistance in order to improve memory device performance. We present evidence of ballistic transport of energy carriers as the characteristic length of the device is decreased to less than the mean free paths of the electrodes carriers. In addition, we investigate the thermal properties of $Ge_2Sb_2Se_4Te$, one of the most promising material candidates for integrated photonics, and show that upon substituting tellurium with selenium, the thermal transport transitions from an electron dominated to a phonon dominated regime. By implementing an ultrafast mid-infrared pump-probe spectroscopy technique that allows for direct monitoring of

electronic and vibrational energy carrier lifetimes in these materials, we find that this reduction in thermal conductivity is a result of a drastic change in electronic lifetimes of $Ge_2Sb_2Se_4Te$, leading to a transition from an electron-dominated to a phonon-dominated thermal transport mechanism upon selenium substitution.

AA-TuP-30 Comparison of the Insulating Properties of Aluminum Oxide (Al_2O_3) High-K Layers at the Early Growth Stages of by Thermal- and Plasma-Enhanced Atomic Layer Deposition on AlGaN/GaN Heterostructures*, **Raffaella Lo Nigro**, E. Schilirò, P. Fiorenza, G. Greco, F. Giannazzo, F. Roccaforte,* CNR-IMM, Italy

A comparative study of the early growth stages of aluminium oxide (Al_2O_3) thin dielectric layers deposited by thermal and plasma-enhanced atomic layer deposition (i.e. T-ALD and PE-ALD) methods on AlGaN/GaN heterostructures is presented and two different nucleation processes have been identified. Investigation has been carried out at nanoscale by morphological and leakage current maps, which showed that the Al_2O_3 thin films deposited by the PE- ALD possess excellent insulating properties, conformal interface with AlGaN/GaN substrate, low oxide trap charges and good dielectric permittivity of $k \approx 8$. By contrast, a not conformal and uniform insulating behaviour has been recorded on T-ALD Al_2O_3 films. The different insulating behaviour and its evolution upon increasing the film thickness is indication that two different growth mechanisms are running and chemical characterization by X-ray Photoelectron Spectroscopy provided evidence that the PE-ALD process occurs under an ideal layer-by-layer growth because of the efficiency the O_2-plasma agent which acts directly on the Al precursor. The T-ALD process by contrast, shows a behaviour similar to the island growth model because of the formation of undesirable Al-N-O bonds. The origin of interface defects, whose limitation is crucial for the correct operation of the device, has been discovered and studied, as well as, the proper deposition process has been defined.

AA-TuP-31 Amorphous ALD Alumina On a Quartz Plate Enables Significant Cost of Ownership (CoO) Reduction in Metal Plasma Etch Chambers*, **Jeff Young**,* Intel Corporation*; G. Mata-Osoro, P. Spring,* INFICON Ltd., Liechtenstein*; J. Delle Donne,* Ultra Clean Technologies (UCT)*; R. Parise,* Ultra Clean Technologies*; V. Venkatesan,* Ultra Clean Technologies (UCT)

Crystalline Al_2O_3 by-product and trace metals deposited on quartz parts in metal etch chambers are a problem. They peel off and cause particle problems leading to unscheduled downtime of chambers. It is therefore important to remove these by-products and trace metals from the quartz parts on a regular basis during preventive maintenance (PM). However, stripping crystalline Al_2O_3 (and trace metals) from quartz without attacking the quartz substrate is a challenge. In order to address this problem, these quartz parts with a specified surface roughness were coated with 200 nm of amorphous ALD Al_2O_3 films. After processing in chamber, these coated parts with by-products were taken out during PM. They were grit blasted to loosen the surface, a proprietary chemical strip developed to remove the ALD Al_2O_3 film and by-product deposition. Quartz substrate showed no degradation as characterized using XRF, particle level and roughness measurements. This process is now qualified, and the recycled quartz parts provide > 75% reduction in Cost of Ownership (CoO) compared to that of new parts.

Fig.1 Shows a TEM cross-section of the stack on top of the quartz plate used in the metal etch chamber after etch residue by-product deposition.

Fig.2 Depicts the process flow for recycling the quartz plate.

Fig.3 Shows the XRF characterization of post-strip and clean surface showing no trace of coating and by-products.

See attached document for the figures.

AA-TuP-32 Application of Powder Atomic Layer Deposition to Solid Oxide Fuel Cell Electrodes*, **Sung Eun Jo**, H. Kim, B. Yang, J. An,* Seoul National University of Science and Technology, Korea (Republic of)

Atomic layer deposition(ALD) can uniformly coat conformal films on complicated structures with atomic-level thickness controllability. ALD is being widely used in the semiconductor industry but is also showing high potential as an effective technique for upgrading electrochemical energy devices' performance and durability by precisely and conformally overcoating their components. For example, the electrodes of solid oxide fuel cells (SOFCs) usually adopt nano-porous and complex structures for fast electrochemical kinetics; to fabricate such porous structures, SOFC electrodes are fabricated by sintering powder materials. Lanthanum strontium cobalt ferrite (LSCF) powder, for instance, is a popular material for SOFC cathode. In LSCF-based electrodes, strontium in perovskite material segregates at elevated temperature (e.g., the operating temperature range of >600C for SOFCs). Exsolution of Sr forms SrOx at the surface of the cathode, which diminishes ORR activity and escalates polarization resistance by blocking active sites at electrodes' surface. Therefore, the conformal and ultra-thin protective coating of LSCF powders is crucial for the stable operation of SOFC electrodes at elevated temperatures.

In this study, we report on the use of powder ALD process to conformally coat LSCF powders for SOFC cathodes. Bare LSCF powders are ball-milled, situated in the rotary module assembled with the ALD station, and are coated with ALD ZrO_2. As powders have an extremely high area-to-volume ratio, static exposure mode for precursor infiltration between nanoscale air gap. In the electrochemical test, the cells with bare LSCF cathodes (no ALD), LSCF cathodes with conventional ALD (C-ALD), and with powder ALD (P-ALD)-coated ZrO2 overcoats are compared. Powder ALD treated cell effectively suppress Sr ex-solution in the entire location of the electrode, and eventually result in the highest maximum power density among cells.

AA-TuP-33 Evaluation of Temporal vs. Spatial Atomic Layer Deposition Techniques for the Production of Ceramic Nanofiltration Membranes*, J. Peper,* University of Twente, Netherlands*; H. Jain,* TNO/Holst Cent, Netherlands*; M. Nijboer, A. Nijmeijer, F. Roozeboom, A. Kovalgin, **Mieke Luiten-Olieman**,* University of Twente, Netherlands

Today's bulk chemical separation and purification is mainly driven by thermal processes like distillation, drying and evaporation. Examples are in hydrocarbon separation from crude oil feedstocks, surface and wastewater purification and desalination. These processes account for 10–15 % of the global energy consumption [1].

As an inherent non-thermal process, membrane-based separation can cause a paradigm shift in worldwide energy consumption since this alternative requires 2 up to 10 times less energy, and will offset carbon emissions correspondingly [1]. However, the challenges in manufacturing large-scale membrane systems are manifold. Bulk wastewater streams can contain solvents that make polymeric membranes unsuitable due to the destructive solvent-membrane interactions. In addition, the production of ceramic membranes for nanofiltration applications with pore sizes typically ranging from ~1 to a few nm is challenging [2,3]. Therefore, new methods for upscalable production of robust ceramic nanofiltration membranes are required.

The potential of applying Atomic Layer Deposition (ALD) in order to narrow down ceramic membrane pores to the nanofiltration range is studied. The aim was to get a better understanding of ALD on 3D porous substrates compared to the state-of-the-art process on planar silicon wafers. Experiments were performed to tune the most important process parameters using different types of ALD reactors – temporal (PICOSUN® R200) and spatial [4]. The advantage of temporal ALD in the production of ceramic membranes is that process recipes proved to be easily tunable, whereas the spatial ALD benefited from high throughput.

A decrease in pore size of γ-alumina membranes was observed for recipes with an increasing number of s- and t-ALD cycles; from 2.5 nm to <0.5 nm within 25 ALD cycles. We also observed a higher growth rate for porous γ-alumina substrates as compared to the reference silicon wafers (GPC 0.14 vs 0.10 nm/cycle).

This study showed the potential of ALD for the production of ceramic nanofiltration membranes by narrowing ceramic ultrafiltration membranes. Furthermore, this exploratory work provides a starting point for further research into the method and showed the importance of directly characterizing the porous substrates. New ALD process recipes specifically aimed at porous substrates can lead to further improvement of the method.

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AA-TuP-34 Robust YF_3 Batch ALD Process With a Novel Precursor for Plasma Etch Tool Component Protection, *J. Kalliomäki, E. Manninen, J. Mariam,* ***Peter King****, R. Ritasalo,* Picosun Oy, Finland

Atomic layer deposited corrosion barrier solutions have been of high interest lately in the semiconductor industry. The main driver for this has been the need to protect plasma etching tools used in several manufacturing steps from self-damage and contamination. Traditionally, thick ceramic coatings applied with spray coating have been used but these techniques suffer from low conformality, which makes it unable to protect parts with complex geometries like showerheads. [1]

The most sought-after materials, like Y_2O_3 and YF_3 are very etch resistant [2], but are difficult to scale to large ALD tools, while retaining good conformality and repeatability [3]. YF_3 especially has been problematic from a tool maintenance and health & safety perspective as available processes involves HF as a reaction by-product.

We present process development and scale up results from a new precursor (*Y-Beta', Air Liquide*), which can produce pure YF_3 films using O_3 as co-reactant. The process is scaled up to Picosun P-1000 class tool with maximum usable chamber volume 0.2 m^3, which can be used to deposit several full-sized showerheads. In wafer batch tool (P-300B) the process can reach a GPC of ~0.6 Å and cycle time <5 s. With 20 s cycle time a Chip-2-Chip uniformity of 3% can be achieved (statistics extracted from mapping spectroscopic ellipsometry measurements). The compositional purity of the resulting films were determined with ToF-ERDA along with structural characterization by XRD.

The general ALD process portfolio has been wanting for a simple, convenient, and robust alternative for YF3 deposition in addition of the two existing ones [4-5]. This new precursor answers directly to this need by allowing the YF3 to be deposited in industrial scale without HF.

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AA-TuP-35 Surface Modification of Atomic Layer Deposited Metal Oxides: Vapor-Phase Grafting of Functional Silanes, ***Vepa Rozyyev,*** University of Chicago*; R. Pathak, R. Shevate,* Argonne National Laboratory, USA*; J. Murphy,* University of Chicago*; A. Mane,* Argonne National Laboratory, USA*; S. Sibener,* University of Chicago*; J. Elam,* Argonne National Laboratory, USA

Covalent surface modification of oxides with alkyl silanes is one of the most commonly used method to prepare well-defined functional surfaces. Using alkyl silanes with functional groups at the alkyl chain will produce functional surfaces for various applications such as water treatment, biosensing, and anti-fouling surfaces. Atomic layer deposition (ALD) is a highly versatile surface functionalization technique that can conformally coat both planar and porous substrates. Surface modification of ALD films with organic species is an ideal way to tailor the surface properties. Here we demonstrate the vapor-phase grafting of various bifunctional silanes on ALD metal oxides. We investigate the grafting of six different silanes with amine, thiol, nitrile, and ester functionalities at 100 °C, 150 °C, and 200 °C temperatures. In situ quartz crystal microbalance (QCM), Fourier-transform infrared (FTIR) spectroscopy measurements, ex-situ atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) measurements show the uniform monolayer silane formation through self-limiting reactions. It is shown that the density of reacted silanes and surface hydrophobicity can be tuned by using different bifunctional silane agents, on different metal oxides, at different temperatures.

AA-TuP-36 Developing ALD RuO_x Process for Coating Porous Current Collectors for Supercapacitor Applications, ***Sakeb Hasan Choudhury,*** LAAS-CNRS, France*; G. Vignaud,* Université Bretagne Sud, France*; P. Dubreuil, D. Pech,* LAAS-CNRS, France

Atomic Layer Deposition (ALD) is considered to be one of the most conformal thin film deposition techniques. In literature, its self-saturated growth mechanism and atomic layer control has been studied in various methods [1]. However, the permeation of ALD into different research fields has brought new challenges in front of us and we investigate such a scientific issue in this work. The application of independent autonomous microelectronic devices has revolutionized the IoT (Internet of Things) based industry [2]. Therefore, the development of onboard micro-energy storage has become one of hot research topics in the scientific community. In recent years, it was evident that the 3D micro-supercapacitors are shaping up to be capable of serving such purposes. One of the remarkable aspects of 3D micro-supercapacitors was the emergence of dynamic hydrogen bubble template (DHBT). It provided the necessary 3D architectures of micro-supercapacitors for satisfying the energy storage requirements of high-power onboard devices. However, the efficient utilization of these highly porous DHBT structures still remains a challenge when it comes to coat them with active materials [3]. Here, in this work, we channel our efforts to utilize the conformal coating capabilities of ALD to handle such challenges. To investigate the scheme, we propose to deposit a hydrous $RuO_2.xH_2O$ as the active materials on DHBT samples. In order to develop the conformal ALD growth, we used $Ru(EtCp)_2$ and O_2 as precursors [4]. The temperature for ALD deposition was kept at 200 C to avoid losing the electrochemical area of the DHBT samples. From our initial experiments, we observed that a capacitance value of 7mF can be achieved from 500 ALD cycles of RuO_x on an Au DHBT template. To study and optimize the conformality of RuOx deposition, an additional trap timing was introduced during the pulsing of the $Ru(EtCp)_2$ precursor.

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AA-TuP-37 Defect Engineering in Corrosion Protected Semiconductor Photoanodes by Atomic Layer Deposition of Titania, ***Oliver Bienek****, B. Fuchs, M. Kuhl, D. Silva, T. Rieth, A. Henning, I. Sharp,* Walter Schottky Institut and Physics Department, Technische Universität München, Germany

Protection layers are important for enabling stable and efficient photoelectrochemical energy conversion, especially for photoanodes operating under highly oxidizing conditions. Although TiO_2 protection layers have been intensively investigated, there are conflicting interpretations regarding the mechanism of charge transport through the films, with some studies indicating hole transport through a defect band in "leaky" titania (TiO_x) and other studies suggesting electron injection from the electrolyte into the conduction band followed by recombination at the Si/TiO_x interface. To shed light on the interfacial transport pathway, as well as elucidate the role of interfacial insulating oxide between absorber and protection layer, we have systematically investigated the effect of ALD process parameters on interfacial charge injection and photoelectrochemical function. In this context, six different ALD processes were established using two Ti precursors, TDMAT and TTIP, both in thermal (H_2O) and two plasma-enhanced (OP) processes, wherein oxygen plasmas of 300 W and 5 W power are applied. To investigate the defect properties of the TiO_x films, optical absorption coefficients were determined using photothermal deflection spectroscopy. The obtained absorption spectra vary over three orders of magnitude in the sub-bandgap region, implying a significant variation of the mid-gap defect concentrations in these films. TiO_x deposited using H_2O as oxidant yields substantially higher sub-bandgap absorption compared to PE-ALD films. XPS measurements not only deliver a direct proof of these mid-gap defects but also reveal a significant amount of Ti^{3+} states for the most defective layer, which suggests that oxygen vacancies are the dominant defect type. Photoelectrochemical characteristics of Si-based electrodes with TiO_x protective coatings, onto which Ni oxygen evolution reaction catalysts have been applied, were determined in 1 M KOH under 1 Sun illumination. While the $Ni/TiO_x/Si$ photoanodes formed using both H_2O and 5 W oxygen plasma as the oxidant feature relatively low onset potentials and light-saturated photocurrent densities, the samples made from 300 W oxygen plasma processes have large onset potentials and shallow slopes indicative of a high series resistance due to oxidation of the Si substrate, as determined by in situ spectroscopic ellipsometry. Among the other samples, which possess comparably thin silica interlayers, we find that the photoelectrochemical onset potentials are correlated with the mid-gap defect concentrations within the ALD layers, providing a route towards rational defect engineering of protective photoelectrode coatings.

AA-TuP-38 Film Characteristics of Lanthanide Oxide Thin Film by Using Atomic Layer Deposition Method*, **Suin Kim**, M. Kim,* EMD Performance Materials, Korea (Republic of)*; S. Ivanov,* EMD Performance Materials

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 films by atomic layer deposition (ALD) with as-deposited 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(iso-propylcyclopentadienyl) terbium(III) ($Tb(^iPrCp)_3$) and Tris(iso-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. ALD thermal window, and the 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 above 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 using TiN/TbO_x or GdO_x/TiN (MIM) structures.

In conclusion, we conducted atomic layer deposition of TbO_x and GdO_x films and analyzed those properties. Both processes showed thermal ALD at 200 ^oC withgood step coverage. The films are expected to be used in applications such as high-k gate insulators or hard mask for complex pattern.

AA-TuP-39 Advanced 3D Mxene ALD Assembly Through Precious Metal Conformal Coating for Clean Energy Applications*, **Debananda Mohapatra**, Y. Kim, Y. Park, S. Kim,* Yeungnam University, Korea (Republic of)

MXenes are a large family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides, with similar and better overall physicochemical properties than one of the most studied 2D graphene. Notably, its electronic and electrochemical properties are massively affected by how these MXene materials are synthesized and processed wet chemically. To eliminate one of the pressing face-to-face staking issues of these MXenes, we try to introduce an atomic layer deposition (ALD) technique to introduce the precious metals conformally. Precious metal like iridium is quite rare and expensive; hence, precise quantity and quality control are desired. These ALD processed precious metals could be fascinating to explore their electrochemical activity along with the novel engineered MXene host material. We also discuss another exciting fullerene family of carbon materials such as carbon nano-onions (CNO), which are multi-shelled cage-like graphitic structures at an intergraphitic distance of 0.34 nm, mimicking onion morphology is excellent host materials for precious metals. Additionally, we will introduce the role of precious metals such as Ir, Pt, Ru ALD induced electrochemical behavior. The novel proposed MXene-ALD noble metal nanostructures could be potential electrocatalysts for HER/OER applications.

AA-TuP-40 Toward a Rational Surface Texture Designof FBR-ALD Pt/CCatalyst to Enhance PEMFC Performance*, **Ji-Hu Baek**, S. Kwon, S. Lee,* Pusan National University, Korea (Republic of)

Proton exchange membrane fuel cell (PEMFC) is an efficient electrochemical energy conversion device that directly generates electricity from the chemical energy of fuels without the emission of greenhouse gases. The most reliable catalyst in PEMFC is Platinum (Pt) metal nanoparticles (NPs) that exhibit excellent electrochemical activity and stability compared to other catalysts. However, using of Pt catalyst is limited due to its very high cost and low abundance on Earth. Therefore, it is important to use Pt catalyst efficiently for making the PEMFC economically viable. In this regard, several synthesis techniques have been developed to reduce the loading and uniform distribution of Pt NPs on carbon support with high electrochemically active surface area (ECSA). One of the most efficient techniques to uniformly deposit Pt NPs with a controllable size on carbon support is to use a fluidized bed reactor (FBR) atomic layer deposition (ALD). Our group recently demonstrated that FBR-ALD Pt/C catalysts can exhibit high fuel cell performance and high endurance even with low Pt NPs loading by optimizing the surface of carbon supports combined with proper ALD process parameters [1]. However, it is still challenging to further improve the fuel cell performance by rational designing the Pt NPs surfaces in order to make FBR-ALD into a viable commercial production.

In this study, a unique way to improve the fuel cell performance was suggested to design and optimize atomic scale surface textures of Pt NPs. During the FBR-ALD of Pt NPs, in-situ surface modulation of Pt NPs were applied via a proper protective oxide deposition and etching. A careful surface studies was performed to analyze the surface morphology, distribution and uniformity of Pt NPs. Electrochemical performances were evaluated and optimized by measuring cyclic voltammetry (CV) and oxygen reduction reaction (ORR). Finally, a fuel cell performance was studied through membrane electrode assembly (MEA) characteristics.

AA-TuP-41 Plasma Enhanced Atomic Layer Deposition (PEALD) of Silicon Nitride for FEOL Applications*, **Marco Lisker**, M. Kalishettyhalli Mahadevaiah,* IHP Frankfurt (Oder), Germany

Silicon nitride (SiN) is commonly used for spacer formation for various gate CMOS-architectures and advanced 3D-RF-devices as heterojunction bipolar transistors as wellas a masking layer in high selective wet etching steps in FEOL processes. Standard processes for SiN like low pressure chemical vapor deposition (LPCVD) results in high quality layers but at the cost of a very high thermal budget. Plasma enhanced chemical vapor deposition (PECVD) results in high quality layers as well but comes with a disadvantage of poor step coverage. The deposition temperatures of PECVD SiN can be much lower compared to LPCVD SiN process which results in lower thermal budget. However, PECVD process leads to plasma damage in the underlying device structures due to the ion bombardment during the deposition step using high RF power. As an appropriate alternative the PEALD process make use of several advantages as lower deposition temperatures, uniformity and conformality of the deposited layers and good step coverage. Hence, in this work we investigate the deposition of SiN using PEALD process and the possibility of the process competing with industry standard LPCVD and PECVD SiN processes.

The deposition process of PEALD SiN is carried out using a high vapor pressure precursor Trisilylamine (TSA). The PEALD deposition parameters which could be varied are identified and the design of experiments (DOE) is systematically carried out by varying only one parameter at a time. The process parameters such as deposition temperature, plasma exposure time, precursor feed time, RF power etc. are among the many other parameters which are used for DOE. Further, the SiN deposition process is investigated by using nitrogen (N_2) or ammonia (NH_3) as the reactant gases. The quality of the deposited SiN layers is investigated in terms of the layer uniformity, refractive index, step coverage, conformality, chemical composition of the layers etc. through various metrology techniques. Additionally, the etch rates of the deposited SiN layers are tested in liquid etchants like hydrofluoric acid and hot phosphoric acid to evaluate the potential of the PEALD SiN layers as high selective wet etch mask.

AA-TuP-42 Mechanical and Optical Properties of Alumina Doped Hafnia Deposited by Plasma Assisted Atomic Layer Deposition*, **Taivo Jõgiaas**,* University of Tartu, Estonia

Atomic layer deposited hafnium oxide is known as high-k material, but could be used as an optical coating. The latter could also require a certain mechanical resilience. Doping could induce phase changes, for instance, stabilizing hafnia in a certain crystallographic phase such as tetragonal or cubic.

Alumina doped hafnia thin films were atomic layer deposited using oxygen plasma as the oxygen source, and trimethylaluminium and tetrakis(ethylmethylamino)hafnium as respective metal sources. The processes were conducted mainly at substrate temperatures of 300 °C with some additional depositions at 200 °C or 400 °C. Elemental and crystallographic phase compositions, optical and mechanical properties were characterized. The film thicknesses averaged around 70 nm.

Correlations between compositions, optical and mechanical properties were drawn, which is essential in tuning optical coatings with certain mechanical properties.

AA-TuP-43 Al Doped Zno Thin Film on High Aspect Ration Structure (1:10) by Ald Process for Biomedical Application*, **Po-Tsung Hsieh**, T. Tsai, T. Wang, C. Lin, T. Chen, H. Tu,* Core Facility Center, National Cheng Kung University, Taiwan

The determination of dopamine (DA) has been used as an important biochemical indicator for progressively degenerative diseases in the central nervous system, such as Parkinson's disease (PD). As compared to the optical sensing techniques for precise DA quantification, electrochemical biosensors provide an attractive technique to analyze the content in a biological sample due to the direct conversion of a biological event to a redox current signal. Based on these categories of procedures occur at the surface of the working electrodes, the enlargement of sensing surface area is a critical factor corresponding to the improvement of sensitivity. The main limitations from insufficient reproducibility and poor stability for the present nanomaterial remain to be solved due to its complicated process of materials coated onto the electrode surface.

For increasing the sensing surface area to enhance the sensitivity, an ultra-sensitive electrochemical biosensor can be realized by the three-dimensional (3D) nano-rod architecture with a remarkable conductive material on it. Nano-rod with high aspect ratio of 1:10 was fabricated. Aluminum-doped zinc oxide (AZO) thin-film with a prominent electrical conductivity is selected for depositing on the surface of nano-rod. The uniformity issue is the key concern especially for the 3D nano-rod structure among many depositing techniques. The uniformity of AZO film will have great impact on the sensitivity of electrochemical sensor. To overcome such issue, atomic layer deposition (ALD) technique was selected for depositing AZO thin film on the nano-rod structure. ALD is a chemical deposition technique relied on the saturated surface reactions and self-limiting which can provide excellent conformality for the deposited thin film. Then AZO thin film was deposited at 250℃ by ALD technique. Trimethylaluminum (TMA) and diethylzinc (DEZn) were used as the precursors for AZO film by ALD process. The deposition sequence (1:9, 1:19, 1:29) of TMA and DEZn was designed for seeking the optimal doping ratio. The processing cycle is 500 times for obtaining the expected AZO thickness of 50nm. After ALD processing, the thickness and uniformity of AZO thin film were continually measured for confirming the thickness at the top and the bottom of the nano-rod. And the doping ratio was also examined for understanding the ALD depositing parameter. The results shows that the resistivity can be obtained by the doping ratio of 1:29 (TMA:DEZn) is 5E-4 ohm-cm. The sensitivity will then be tested on the electrochemical sensor. This study proposed microfabrication would be further conducted into the other electrochemical sensors in the future.

AA-TuP-44 H_2 Separative Membrane Fabricated by Thermal Atomic Layer Deposition*, **Clémence Badie**,* Aix-Marseille University, France*; M. Drobek,* CNRS- Univ. Montpellier, France*; M. Bechelany,* CNRS/Univ. Montpellier, France*; J. Decams,* Annealsys, France*; L. Santinacci,* Aix-Marseille University, France

To provide affordable H_2 with high purity for energy applications, new strategies as H_2-selective membranes gained in interest. This technology presents valuable benefits as it is cost-effective and have a reasonable environmental impact. In addition, a large variety of materials is available, thus, the composition of the membrane can be adapted to the working conditions. This study focuses on the fabrication of dense membranes able to operate at the high temperatures required in industrial processes (400-800°C). The specificity of the present approach is to fabricate new nanocomposite devices that combine the stability of a ceramic matrix, titanium nitride, with the catalytic effect of palladium nanoparticles used as nanofillers. Both TiN films and Pd nanoparticles are deposited onto a hetero-porous alumina tubular membranes by thermal Atomic Layer Deposition (ALD). The composite membrane is optimized to reach the highest H_2-selectivity (purity) and permeation (flow), by finely tuning the thickness and the chemical composition of the TiN/Pd coating. ALD is an original technique in this field, but it is well adapted because it allows for coating nanostructured substrates with an excellent control of the thickness and composition.

The fabrication of the membrane follows two steps. First, the TiN deposit fills the alumina porosity. The coating forms a dense layer on the nanoporosity at the inner part and penetrates into the macroporosity of the outer part, covering the alumina grains. Afterwards, the Pd nanoparticles are deposited. The selectivity and the permeation of the TiN-Pd membrane are assessed using H_2, He and N_2. The increase of the temperature up to 400°C allows for achieving an encouraging H_2 ideal selectivity and permeance of 35 and 258 GPU (Gas Per Unit), respectively. Moreover, these values increase during the measurement: the selectivity and the permeance rises up to 109 and 718 GPU, respectively, after 4.5 h at 400°C. These performances are promising as a similar pure Pd membrane presents an ideal selectivity of 23 and a permeance of 991 GPU at 188°C [1]. The investigation of the thermal evolution and the stability of the present membrane is then required. Complementary results will therefore be presented.

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AA-TuP-45 Universal Relationship between Spontaneous Polarization and Coercive Field of HfZrO Ferroelectric*, **Min Liao**, J. Xiang, X. Wang,* Institute of Microelectronics, Chinese Academy of Sciences, China

The discovery of ferroelectric characteristics in doped HfO_2 films strongly supports the ferroelectric transistors as a nonvolatile memory device. The ferroelectric characteristic is key. However, this issue is still not completely understood. In this work, we investigate the relationship between the spontaneous polarization and the coercive field of HfZrO ferroelectric. We grew the HfZrO film by changing atomic stoichiometry, annealing temperature and time, insertion dielectric material (HfO_2, ZrO_2, TiO_2, Al_2O_3) by ALD method. We find a universal relationship between spontaneous polarization and coercive field of HfZrO ferroelectric, regardless of growth condition and ferroelectric/dielectric structure. This is helpful to understand the HfZrO ferroelectric.

AA-TuP-46 Synthesis of Noble Metal Nanoparticles by ALD for Electrocatalysis*, **Sitaramanjaneya Mouli Thalluri**, R. Zazpe, H. Sopha, J. Macak,* University of Pardubice, Czechia

Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance in various catalytic applications.[1] Due to their scarcity efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique that is available to reduce the metal loading of noble metals.[2],[3] ALD is employed to develop continuous thin films of thickness down to single atom. Due to the governing surface energies variations for noble metals with respect to substrate surface, the growth initiates as nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films.

For electrocatalytic applications, it is important to choose the right substrates. Among available substrates, Carbon papers (CP) and Titania nanotube (TNT) layers are best choices considering their properties, availability, vast literature and low costs incurred using these as support substrates in electrocatalysis and photocatalysis. Several surface modifications for CP's and variations on morphological aspects of TNT layers had received a great attention form applied fields due to their improved surface area, conductivity and stability.[4],[5][6] Anodic oxidation of titanium foils using relevant electrolytes is one of the appropriate method to fabricate TNT layers.[7] Uniformly decorating these CP's and TNT layers by nanoparticles or thin films of catalysts proved to be highly efficient with no boundaries on applications.[8]

ALD is the most suitable technology that can decorate high aspect ratio and high surface area nano architectures.[9]

The presentation will introduce and describe the synthesis of different noble metals by our ALD tool (Beneq TFS 200) on various aspect ratio TNT layers and CP substrates. It will also include the corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

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AA-TuP-47 Protection of Platinum Electrocatalysts for Water Electrolysis Using Atomic Layer Deposited Silicon Dioxide*, **Ming Li**, R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Hydrogen is an important building block for the energy transition because it is a clean renewable energy carrier and an important feedstock for the chemical industry[1]. Among the various methods of producing hydrogen, water electrolysis using electricity from renewable sources such as wind and solar will become a main pathway in the coming years. Platinum is one of the most effective electrocatalysts for water reduction to hydrogen and hydrogen oxidation and is widely used in the PEM electrolyzers and fuel cells. However, its high costs and scarcity limit its application. To use platinum-based electrocatalysis in a cost-effective manner, it is crucial to have a method to protect the platinum catalyst from degradation and prolong its lifetime.

Here, we have applied an atomic layer deposited SiO_2 coating on the surface of platinum electrocatalysts to improve its durability. TEM, XPS, SEM-EDS mapping were used to characterize the catalyst. Linear sweep voltammetry (LSV), cyclic voltammetry (CV), and accelerated durability tests were applied to study the stability of the catalyst. We found that after 1000 cycles of CV scans in the water reduction potential range, the current density at -0.2 V vs. reversible hydrogen electrode (RHE) of the original catalyst was reduced by 34%. By contrast, after applying 2 cycles of ALD SiO_2 deposition, the current density at the same voltage was reduced by 7.3% after the same test procedure. After applying 5 cycles of ALD SiO_2 deposition, the catalyst current density was only reduced by 1.9% after the accelerated durability test. The particle size of the original catalyst increased by 16% after 1000 cycles CV scans, whereas it only increased by 1.6% after 1000 cycles scans protected by 5 cycles of ALD SiO_2 deposition.

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AA-TuP-48 ALD-Deposition of Cathodic Materials for 3D Li-Ion Micro Batteries - Ongoing Results*, **Antoine Peisert**, G. Lamblin, D. Lenoble, N. Adjeroud,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Since their discovery in the 70's, Li-ion batteries are a hot topic in R&D, driving innovation and investigation of new materials and synthesis routes to meet the market demand. Widely use over a large range of applications (smartphone, laptops, electric vehicles), Li-ion batteries face numerous challenges: enhancement of the electrochemical properties, miniaturization, increase in safety… Among the solutions considered to answers those challenge, the use of 3D microstructures could potentially increase the active specific surface, in regard to a fix volume, thus enhancing the capacity of the battery and its energy density.

The approach presented in this oral presentation is the use of ALD (Atomic Layer Deposition) to deposit a thin film of cathodic material ($LiCoO_2$) onto and into a porous 3D membrane. By utilizing ALD supercycles (a combination of one Li-based ALD process to form Li_2CO_3 and another Co-based ALD process to form Co_3O_4), a thin film of $LiCoO_2$ is obtained, with the numerous benefits of ALD processes, like total covering of the surface, homogeneity, uniformity and conformality on high aspect-ratio structures. A similar approach has been developed in the literature using PE-ALD, but to the best of our knowledge, no other source are using thermally activated ALD processes.

This process would allow the uniform deposition of active electrochemical material on 3D substrate, thus developing 3D Li-ion batteries.

This presentation will gather the results obtain for the fabrication of Co_3O_4 and Li_2CO_3 thin films onto planar substrates by thermal ALD, characterized by Raman spectroscopy, XPS (X-Ray Photoelectron Spectroscopy), and EDX (Energy Dispersive X-Ray), as well as thickness measurements obtain by mean of XRR (X-Ray Reflectivity) measurements. Then, supercycles results combining both previous cycles will be shown, with the same type of physico-chemical characterizations, as well as some of the first evaluations of the electrochemical performances of the developed electrodes

AA-TuP-49 Disentangling the Effect of Diffusion and Solubility in the Gas Barrier Properties of ALD Alumina Thin Films*, S. Bhudia, J. Barbe, M. Gerard,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; V. Cassio,* MET-LUX S.A., Luxembourg*; **Renaud Leturcq**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Alumina thin films deposited by ALD have demonstrated very good barrier properties [1] due to the expected low pinhole density as compared to films deposited e.g. by CVD, enabling long-term stability of photovoltaic [2] and OLED devices [3]. However, the obtained permeation properties strongly depend on the deposition temperature and the substrate [4], the origin of which are still not fully understood. In particular, the effect of pinholes as compared to bulk diffusion properties of the ultra-thin film are not fully elucidated. Here we address the potential permeation mechanisms in alumina thin films deposited by ALD by using time-dependent analysis of the helium permeation rate.

We compare two alumina thermal ALD processes, standard process using trimethylaluminium (TMA) and water (H2O) as precursors, and a new process where a diethylzinc (DEZ) injection before the TMA injection provides better properties for films deposited at room temperature. Both films are deposited on standard PET films. To address the permeation mechanisms of alumina thin films, we have first compared the water and oxygen permeation properties measured by usual Mocon® test to helium permeation properties measured using an in-house developed prototype. The good correlation of all measurements for alumina obtained using the standard TMA-H2O process shows the high stability of alumina when exposed to water or oxygen, and that the permeation can be well described by the physical diffusion of the gas through the film. A lower correlation is obtained with the new DEZ-TMA-H2O process, which we attribute to higher density of OH groups.

By analyzing the time dependent helium permeation rate, we disentangle the effective diffusion coefficient of the barrier layer and the solubility, showing that the main improvement is obtained by a reduced solubility with only a weak change in the diffusion coefficient. These results have been compared to analytical models and simulations, using both a continuous bilayer model and a defect permeation model. While both models can reproduce well the observed data, the defect permeation model allows us to extract the product between the pinhole density n and their average diameter d_0. We obtain values 10 to 100 times lower than SiOx and SiN films obtained by PECVD [5].

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AA-TuP-50 Vapor Phase Infiltration (VPI) on Polymers Fibers and Fabrics for Multifunctional and Antimicrobial Textile*, **Natalia Chamorro**, M. Knez,* CIC nanoGUNE, Spain

For functional textile the relevant industry is seeking materials with a wide range of exciting new applications such as self-cleaning, antibacterial, anti-odor, etc., ideally at the same time. One of the very promising strategies to implement such properties into textile is the application of vapor phase chemistry to the manufactured textile.

In this work, we present our strategy to functionalize textiles with a mixed composition, namely denim jeans (mix of cotton and polyethylene fibers), with TiO2 and ZnO by applying vapor phase infiltration (VPI). The resulting modified textile becomes largely waterproof, antimicrobial properties and can block UV light. Interestingly, the pristine material is hydrophilic and absorbs water rapidly. However, after treatment with TiO2 the wetting properties change to hydrophobic, which is seen in the increase of the water contact angle. We assign the evolving hydrophobicity to the wetting behavior of the rough surface in the textile. This property can be adjusted by controlling some processing parameters, such as the number of VPI cycles or the exposure time of the textile to the metalorganic precursor. Furthermore, the incorporation of TiO2 into the textile as infiltrating and coating inhibits the attachment of both gram-positive bacteria (Staphylococcus aureus) and gram-negative bacteria (Escherichia coli).

These results suggest that the increment in roughness and the evolving hydrophobicity have a considerable effect on the binding of bacteria to the textile fibers. In addition, an improvement in the UV blocking capacity of the textiles was observed. In this case the material shows the ability to absorb in the UV region from 280 to 400 nm.

The application of VPI to textile can introduce new features to the materials which can synergistically act and contribute to the development of functional textiles.

AA-TuP-51 Impact of Substrate Bias on the Wear Rate of Plasma Enhanced Atomic Layer Deposited TiVN, ***Mark Sowa,*** Veeco ALD*; M. Chowdhury,* Department of Materials Science and Engineering, Lehigh University*; K. Van Meter, T. Babuska,* Department of Mechanical Engineering, Florida State University*; A. Kozen,* Department of Materials Science & Engineering, University of Maryland, College Park*; N. Strandwitz,* Department of Materials Science and Engineering, Lehigh University*; B. Krick,* Department of Mechanical Engineering, Florida State University

During Plasma Enhanced Atomic Layer Deposition (PEALD), substrates are typically subjected to alternating exposures of chemical precursors and plasma generated species including: atomic and molecular radicals; atomic and molecular ions (positive and negative); electrons; and photons. Plasma physics dictate a sheath form at surfaces in contact with the plasma. A potential drop across the sheath develops equilibrating the flux of negative (mostly relatively fast moving electrons) and positive (slower, heavier ions) charge to the surface. During PEALD, energy acquired by positive ions accelerated through the sheath is transferred to the surface of the substrate and growing film playing a role in the resulting substrate/film interface and film properties. Through application of RF power to the substrate holder, the energy acquired by positive ions crossing the sheath from the plasma to the substrate is increased. Recent studies have demonstrated variation of PEALD film properties through application of different RF bias levels. Work continues to elucidate how the potentially important RF bias process knob can be leveraged to provide additional control on PEALD film properties.

We have previously reported on the excellent wear rate properties of PEALD TiN and VN.[1] Our continuing studies have shown superior wear properties for mixtures of these two films compared to the pure binary nitrides. In this study we have investigated how low substrate bias voltages during PEALD impacts film characteristics ultimately focusing on the tribological properties of TiVN.

1:1 TiVN films were deposited in a Veeco G2 Fiji Plasma ALD system with TDMAT, TDMAV, and N_2 plasma at 250°C over a range of low RF bias voltages and durations. We will report on the impact of substrate ion bombardment energy and dose on film properties including wear rate, density, crystallinity, roughness, composition, and stress.

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AA-TuP-52 Thermal and Aqueous Media Stability of $Sr_2Mgsi_2O_7$:Eu^{2+}, Dy^{3+} Phosphors Encapsulated by Al_2O_3 Using Atomic Layer Deposition (ALD), ***Erkul Karacaoglu,*** Karamanoglu Mehmetbey University, Turkey*; A. Okyay,* Okyay Technologies and with the Stanford University*; H. Yurdakul,* Kutahya Dumlupinar University, Turkey*; M. Losego,* Georgia Institute of Technology, USA

This study includes the results of thermal stability and aqueous media studies of $Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+}blue light emitting phosphorescence powders synthesized from solid-state reaction method and Al_2O_3 encapsulation via atomic layer deposition (ALD). Water immersion studies revealed that the uncoated phosphor powders have good resistance to aqueous media up to 30 days. Along with this resistance, there was also stability in the blue phosphorescence (466 nm) characteristics and structural properties. Thermal stability tests up to 1000 °C showed that these phosphors are unstable and loss afterglow property at elevated temperature, thus limiting their applications in the low to high temperature range. ALD coatings of ~10 nm Al_2O_3 on phosphor powders improved the phosphorescence ability by percentage of ~6 and a significant improvement was also observed in phosphorescence stability at high temperatures. This study will undoubtedly create an opportunity for the use of these long afterglow phosphors in applications that require heat treatment process. Successful encapsulation of $Sr_2MgSi_2O_7$-based phosphors will make them possible to utilize in applications requiring heat treatment or in high and continuous temperature environments.

AA-TuP-53 Fabrication of High-Quality Titanium Nitride Thin Film as a Cu Diffusion Barrier Layer by Hollow Cathode Plasma Atomic Layer Deposition at Low Temperature, ***Ha Young Lee,*** *J. Han, B. Choi,* Seoul National University of Science and Technology, Korea (Republic of)

Use of the Cu interconnects in CMOS-based demands advancement of diffusion barrier layers which prevent Cu diffusion into the Si based transistors at the elevated temperature.Titanium nitride (TiN) is one of good candidate for Cu diffusion barrier material among the transition metal nitrides due to its high thermal stability and low electrical resistivity. TiN thin film is usually grown by physical vapor deposition (PVD), and chemical vapor deposition (CVD). As scale down of the feature size, TiN barrier layers are required to be thin and conformal. In this regard, the territory of atomic layer deposition (ALD) can be expanded to achieve high step coverage with high quality. Introducing plasma source to ALD equipment, it is possible to fabricate higher quality thin film at a lower process temperature.Hollow cathode plasma (HCP) source is the latest plasma source to alternate inductively coupled plasma (ICP), capacitively coupled plasma (CCP), and microwave plasma (MP). HCP have the advantages of low plasma damage, high radical and electron density, leading to faster growth rates, improved crystallinity, and scalability.

In this study, TiN thin film was grown by HCP-ALD (HCP source by Meaglow, US and ALD by CN-1, Korea). HCP-ALD process was executed at temperature of 230, 250, 300℃, using Titanium tetra chloride ($TiCl_4$) as Ti precursor and ammonia (NH_3) as reactants with 0.5, 0.55, 0.54Å/cyc at each temperature. TiN thin film has face centered cubic polycrystalline structure and uniform thickness confirmed by XRD and TEM. Density of TiN_x thin films was 5.16-5.29g/cm^3, which showed higher density than that of sputtered TiN, which is similar to the theoretical density (5.35g/cm^3) of TiN. HCP-ALD grown TiN showed a surface roughness of about 1.2nm confirmed by AFM and XRR. Resistivity of TiN was decreased by increasing deposition temperature showing about 160μΩ.cm grown at 300℃ with 35nm-thicnkess. HCP-ALD grown TiN was composed of Ti, N, O (3at%), and Cl (0.01at%) by AES depth profile and ToF-SIMS. Through the XPS analysis, TiN film was mainly consisted of Ti-N with a small amount of Ti-O-N, and no Cl peak was identified. Ti:N ratio was confirmed to 1:0.95 by RBS analysis. The diffusion barrier properties for Cu were evaluated by rapid thermal annealing at the temperature range of 200-800℃. The failure temperature was confirmed about 700℃ at 10-nm-thick TiN thin film between Cu and Si. In addition, the step coverage test was executed at trench wafer with aspect ratio of 7:1, which was higher than 95% for sidewall step coverage.

AA-TuP-54 Adjusting Crystal Structure in an In-Zn-O System Deposited by PEALD and its TFT Application, ***TaeHyun Hong,*** *Y. Kim, J. Park,* Hanyang University, Korea (Republic of)

Oxide semiconductors have been used in various electronic devices because of their low processing temperatures, high mobility (≥ 20 cm^2/Vs), and low off-current characteristics (~10^{18} μA/μm). In particular, since the crystal structure affects electrical properties such as mobility, several studies have been reported for deposit oxide semiconductors with the crystal structure. However, multi-component oxide semiconductors with different crystal structures of each element generally exhibited amorphously, or a high temperature (> 400℃) was required to form the crystal structure. In this study, InZnO (IZO) semiconductors were deposited by plasma enhanced atomic layer deposition (PEALD) at low growth temperature (200℃). The chemical composition ratio was controlled by adjusting each InO and ZnO sub-cycles. By controlling each compositional ratio, the crystal structure of IZO was also influenced. Especially, the c-axis aligned hexagonal structure was also demonstrated in this process. Since the PEALD uses plasma reactants for chemical deposition, we suggest that high plasma energy could induce the crystallization of IZO. For thin film analysis of IZO deposited with PEALD, we conducted X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD). To examine potential use for thin film transistors (TFTs), the IZO film was deposited as an active layer, and inverted staggered- type TFTs were fabricated onto Si substrates.

AA-TuP-55 Pt-coated Si X-ray Optics with Plasma Atomic Layer Deposition for GEO-X Mission, ***Masaki Numazawa,*** *D. Ishi, A. Fukushima, Y. Ezoe, K. Ishikawa, S. Sakuda, T. Uchino, A. Inagaki, H. Morishita, Y. Ueda, T. Murakawa, Y. Tsuji, L. Sekiguchi,* Tokyo Metropolitan University, Japan*; K. Mitsuda,* National Astronomical Observatory of Japan

We have been developing an ultra-lightweight X-ray optic by using MEMS technologies for future X-ray astronomical missions (Ezoe et al., 2010,

Microsys. Tech. 2010, 16, 1633), especially GEO-X (GEOspace X-ray imager) mission which is an 18U CubeSat (~20 kg) project to perform soft X-ray imaging spectroscopy of the entire Earth's magnetosphere from Earth orbit near the Moon (Ezoe et al., 2020, Proc. SPIE 11444, 1144428).

The MEMS X-ray optic is made of 4-inch Si (111) wafer of ~300-µm resultant thickness. The Si wafer is firstly processed by deep reactive ion etching such that they have numerous curvilinear micropores (20-µm width) whose sidewalls are utilized as X-ray reflective mirrors. High-temperature hydrogen annealing and chemical mechanical polishing processes are then applied to make those sidewalls smooth and flat enough to reflect X-rays. After that, the wafer is plastic-deformed into a spherical shape and Pt-coated by atomic layer deposition (ALD) process to focus parallel X-ray lights from celestial objects with high reflectivity. Finally, we stack two optics bent with different curvatures (1000- and 333-mm radius) and complete the Wolter type-I telescope. The telescope is our original micropore optics and possesses lightness (~5 g), a short focal length (~250 mm), and a wide field of view (~4 deg x 4 deg).

We adopted the plasma ALD process to form smooth-thin Pt film on the surface of the micropore on our optic. High-aspect-ratio micropores with 20-µm width and ~300-µm depth were coated with ~20-nm Pt and ~10-nm Al2O3. Measured X-ray reflectivity curves for Al Kα 1.49 keV radiation indicated the surface roughnesses were estimated as 1.2 +0.6/–1.0 and 1.6 ± 0.1 nm RMS before and after the plasma ALD, respectively (Ishi et al., 2020, Appl. Phys. Express, 13, 087001). The surface roughness of the plasma ALD-coated Pt film was comparable with that of the substrate material and better than that of a thermal ALD-coated one in our previous study (Takeuchi et al., 2018, Appl. Opt., 52, 3237). This result and the roughness itself generally satisfied a specification of the telescope for the GEO-X mission. We also optimized the other processes to enable the optics to achieve an angular resolution of ~5.4 arcmins in half-power width (~10 arcmins in half-power diameter required for GEO-X) from the reflective surface figures and the entire wafer shapes. In this paper, we report the enhancement of the Pt-coated Si micropore X-ray optics by using the plasma ALD and the X-ray imaging performance of the telescope as an engineering model for the GEO-X mission (see Fig.1 in Supplemental Documents).

AA-TuP-56 Structural and Optical Properties of Atomically Engineered Ir/Al_2O_3 Heterostructures*, **Pallabi Paul**, P. Schmitt,* Friedrich Schiller University Jena, Germany*; Z. Wang, W. Li, M. Kling,* Ludwig-Maximilians-University of Munich, Max Planck Institute of Quantum Optics, Germany*; A. Tünnermann,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF , Germany*; A. Szeghalmi,* Fraunhofer Institute for Applied Optics and Precision Engineering, Germany

Recently, the search for nonlinear optical materials has experienced tremendous attention. Due to the continuous requirement of shrinking device sizes, 3D photonic integration, the search for new nonlinear optical materials has become increasingly essential as a substitute to commercially available nonlinear bulk crystals. Owing to the advancement of nano-structuring and coating technologies down to atomically controlled dimension and composition, emerging technologies, such as atomic layer deposition (ALD) has enabled the fabrication of new atomically thin nonlinear optical materials.

In this work, we have explored an effective method to deposit atomically thin interfaces of Ir/Al_2O_3 heterostructures by means of ALD. Atomic layer deposition is a chemical coating technology based on sequential and self-limiting reactions of gaseous reactants with the available functional groups on the substrate surface allowing uniform and conformal films on high aspect ratio structures, 3D substrates, and micro-nano structured objects. The Ir/Al_2O_3 nano-stacks are investigated by spectroscopic ellipsometry, UV/VIS spectrophotometry, XRR, GIXRD, XPS, and HRTEM to obtain the structural, and optical properties. XRR and GIXRD measurements along with HRTEM micrograph demonstrate the growth of amorphous layered heterostructures. Additionally, XPS investigations reveal that for ultrathin Ir contributions, there is a formation of IrO_2 at the interface, in contrast to discrete nanoparticle formation. The optical dispersion profiles (refractive index, and extinction coefficient) of the compositions have been reliably determined employing the spectroscopic ellipsometry technique. Upon increasing the Ir contribution, the whole layered stack undergoes a transition from an effective insulating material towards an effectively metallic system at a critical Ir thickness regime of 2-4 nm.

Initially, iridium nanoparticle systems are examined for their nonlinear optical response. We have experienced the presence of third-order nonlinearities in Ir nanoparticles. Furthermore, nonlinear optical measurements show the enhancement of two orders of magnitude in third-harmonic intensity as compared to pure Al_2O_3 layers by the inclusion of Ir within the heterostructures. Further experimental investigations and theoretical validation of third-order nonlinearities are currently in progress.

AA-TuP-57 Broadband Absorbers by ALD: An Opportunity for Solar-Driven Applications*, **Mario Ziegler**, V. Ripka,* Leibniz Institute of Photonic Technology, Germany*; P. Cheng,* TU Ilmenau, Germany*; K. Kc, H. Wagner, U. Huebner,* Leibniz Institute of Photonic Technology, Germany*; D. Wang, P. Schaaf,* TU Ilmenau, Germany

The incorporation of nanoparticles in photocatalytic materials improves the absorption behavior and thus, decreasing drastically the necessary thickness of the functional layers. Moreover, the efficiency can be easily increased by absorbing a larger fraction of the incident light due to optical properties of large variety of different nanoparticles. Nevertheless, the incorporation of many different nanoparticles in photocatalytic materials remain challenging. ALD is a versatile and flexible tool with good controllability of the film composition and the deposition itself, leading to new opportunity in layer design.

Here, we report on a plasma-enhanced ALD process on planar and nonstable substrates to fabricate complex 3D hybrid nanostructures with high absorption above 99 % from 220 nm to 2500 nm (Figure 1 (a)) and peak absorption of 99.77 % at a film thickness of only 9 µm [1]. In contrast to classical ALD, this approach utilizes the metastability of planar substrates within the PE-ALD process. The metastable substrate acts as a time-limited precursor container leading to the generation of complex 3D architectures. The geometry of these hybrid structures can be easily adjusted by the applied PE-ALD parameter. So, sponge-like, highly-porous or nanowire-like structures can be generated [2]. The structures consist of nanoparticles, originated from the planar template, and a 3D scaffold originated from the PE-ALD process. By applying silver as template and silica as PE-ALD material, we have shown the formation of high absorption silver-nanoparticle silica nanowire hybrid layers.

We found that the 3D silica-scaffold leads to a preferential forward-scattering while the Ag-NP leads to broader absorption of the incident light. The excellent optical properties as well as the opportunity to generate a variety of different composition setups might be quite promising for solar-driven applications such as plasmonic-induced photocatalysis, photothermal water purification (figure 1 b) or photovoltaics [3].

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AA-TuP-58 PE-ALD Synthesis and Characterization of Silver Nanoparticles and Ultrathin Films*, **Petru Lunca-Popa**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; S. Guillemot,* ASM, Korea (Republic of)*; R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Owning its superior optical, electrical and thermal properties, silver is used on wide spectrum of applications ranging from devices based on plasmon resonance (Ag NPs) to optical mirrors infrared reflecting coatings. Nonetheless, the Volmer Weber mechanism governing the growth of Ag films make the synthesis of thin continuous Ag films very challenging as it favours islands morphology. Further, due to self-limiting surface reactions, the ALD is established for its ability to produce an accurate and precise thickness control. In this work we present a thoroughly study on the impact of PEALD parameters on the Ag deposition and consequently we demonstrate the self-saturated regime required for obtaining good control of the deposition and large-scale uniformity. A model explaining the Ag NPs growth mechanism correlated with the experimental results is also suggested. This fine control of the Ag NP morphology is of a great interest for applications based on SPR, as those require precise NP dimensions. Finally, we present an original two-step PECVD-CVD synthesis method for fabricating continuous and highly conductive ultra-thin films. The first step provides a uniform new morphology made of compact Ag NPs that is usually not achieved at low thickness with CVD or ALD. The experimental results suggest that the chemical reaction occurs not only on the surface but also in the gas phase. The second step, consisting in plasma post-treatment enhances the electrical conductivity of silver films by increasing the connectivity between particles. Electrical performances are comparable with those describing sputtered films. This novel leads to a high film conformality on complex lateral high aspect ratio structures, with better coverages than the one reported up to now for ALD of Ag. The presence of

an absorbance peak in the visible range is a signature of metallic NP morphology causing localized surface plasmon resonance. By following the film reflectivity spectrum of Ag NP films, a 'continuous-like' behaviour explained by the Drude model is found at low wavelengths whereas higher wavelengths highlight a 'particle-like' behaviour sticking to the oscillator model. This evolution is similar for separated NPs using standard PE-ALD and for the films fabricated using the new approach. The plasma post-processing gives strong increase of the infrared reflectance (up to 97%) and a strong decrease (down to 3%) of near infrared transmittance.

AA-TuP-59 Bipolar and Unipolar Resistive Switching in HfO_2 Based Films Embedding Ni Particles*, **Joonas Merisalu**, M. Otsus, T. Viskus, T. Kahro, A. Tarre, A. Kasikov, P. Ritslaid, J. Kozlova, J. Aarik, K. Kukli, A. Tamm,* University of Tartu, Estonia

Among various thin metal oxide films, studied as resistive switching (RS) media for memristor cells, HfO_2films have been mentioned as media where both unipolar and bipolar RS could be observed dependently on the cell design [1]. Nanocomposites of HfO_2 and foreign metal particles have also been studied as RS media [2]. However, different types of RS that can co-exist in these structures may destabilize RS and complicate programming-reading operations.

In the present work, changes in RS parameters and direction were studied in HfO_2 based films grown using two different ALD processes, based on $HfCl_4$ and O_3, and $Hf[N(C_2H_5)(CH_3)]_4$ (TEMAH) and O_2 plasma [3] as the precursors. Both sample sets contained cells where Ni particles with sizes of around 70 nm were embedded in HfO_2, as well as cells with particle-free HfO_2 films with the same thickness. All films demonstrated bipolar RS (Figs. 1 and 2). In some cases, clockwise and counterclockwise bipolar RS, and unipolar RS were detected in the same device. During endurance tests of some samples, the RS direction changed after several thousand RS cycles (Fig. 3).HfO_2 films grown from $HfCl_4$ demonstrated all three types of RS (Figs. 1, 3, and 5), whereas HfO_2 grown from $HfCl_4$ with Ni particles showed dominantly bipolar RS (Figs. 2 and 4). The endurance tests of the latter samples allowed recording 33000 RS cycles with the ratio between low and high resistivity states (LRS:HRS) of an order of magnitude (Fig. 4). HfO_2grown from TEMAH with Ni particles exhibited unipolar RS with reset voltage below 0.8 V (Fig. 6). The transition to LRS could place gradually. In the latter case intermediate current-voltage loops could be recorded before final transition to LRS (Fig. 6). This could indicate the possibility of multilevel switching.

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AA-TuP-60 Novel Sulfide and Nitride Materials by Plasma Enhanced Atomic Layer Deposition*, **Jakob Zessin,*** SENTECH Instruments GmbH, Germany*; M. Hagel, T. Reindl,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany*; K. Küster,* SF Interface Analysis, Max Planck Institute for Solid State Research, Germany*; P. Plate,* SENTECH Instruments GmbH, Germany

The preparation of thin sulfide and nitride films for electronic applications attracts an increasing interest. Atomic layer deposition (ALD) is an advanced method used to deposit uniform thin films with precisely controlled thickness in the sub-nanometer range, on large surface area substrates and with complex 3D-geometries, which makes ALD an important technique in thin film and device manufacturing.

In this work, we investigate the deposition of Molybdenum disulfide (MoS_2) and Niobium nitride (NbN) as representative layers for sulfides and nitrides, respectively, which are used as active layers in electronic devices. MoS_2 is a 2D–material, which consist of a layered structure and the layers can be exfoliated to a single layer. Vice versa to exfoliation, a defined number of layers could be deposited by ALD. The properties of MoS_2 depend on the number of layers. For example, the band gap changes from 1.3 V (indirect) to 2 V (direct) when reducing the number of layers from bulk to a single monolayer.[1] MoS_2 can be used in manifold applications such as thin film transistors (TFTs), photovoltaic devices and as a catalyst for hydrogen evolution reaction due to its optical and electronic properties. NbN is a superconductor and has a critical temperature of up to 13.8 K.[2] Therefore, it has potential for application in single photon detectors.

The depositions have been carried out in a SENTECH plasma enhanced ALD (PEALD) tool. A PEALD process has been developed for MoS_2 and NbN films by using in-situ ellipsometry (SENTECH ALD Real Time Monitor). Furthermore, the films have been analyzed by ex-situ ellipsometry and X-ray photon spectroscopy to determine the optical parameters and the exact film composition. The film morphology of MoS_2 was investigated by means of scanning electron microscopy.

It is observed that MoS_2 features a saturated growth in the precursor half-cycle, but a clear saturation was not found during the plasma treatment step. The temperature window was determined between 200°C and 300°C. The first XPS results revealed the formation of MoS_2, however, there are some contaminations of carbon and oxygen present in the film.

The NbN film properties were investigated depending on the used gas species, i.e. nitrogen and hydrogen. A correlation between the obtained electrical properties of the films and the used plasma gases was observed. Tuning the plasma gas mixture allows to deposit high quality films at different substrate temperatures.

In conclusion, we show successful PEALD processes for the deposition of MoS_2 and NbN.

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AA-TuP-61 Atomic Layer Deposition of Epsilon Near Zero Transparent Conducting Oxides*, **Emily Duggan,*** Tyndall National Institute, University College Cork, Ireland*; D. Ghindani,* Tampere University, Finland*; J. Lin,* Tyndall National Institute, University College Cork, Ireland*; H. Caglayan,* Tampere University, Finland*; I. Povey,* Tyndall National Institute, University College Cork, Ireland

An epsilon-near-zero (ENZ) material, in which the real component of the permittivity vanishes, exhibits distinct optical features such as large nonlinearity, near-zero refractive index, decoupling of electricity and magnetism, and infinite phase velocity. Furthermore, it has been shown that the refractive index of these transparent conductive oxides can be altered dramatically when light, with a large enough intensity and close to the plasma-resonance frequency (ENZ frequency), impinges on a layer of a few tens of nm-thickness, these changes are rapid and reversible, with the material being excited and returning to its original state on a timescale of a few picoseconds. Such properties give ENZ materials the potential to revolutionise ultrafast photonic devices.

In this study we have used atomic layer deposition (ALD) to realise ENZ characteristics in doped ZnO. All growth was performed in a Picosun R200 in thermal mode, using Diethylzinc, Tetrakis(dimethylamino)titanium and Trimethylaluminium as the metal sources, and water as the co-reagent. Doping was performed using a laminate methodology. The ENZ frequency was tuned by varying growth parameters, thickness, and doping ratios to optimise the response at the communication wavelength of 1.6 micron. The use of ALD to generate an efficient ENZ material is a significant step to realising manufacturable materials that enable efficient light-light interaction-based device technologies.

AA-TuP-62 Magnetic Domain Creation by Local Reduction of Nickel Oxide Films*, **Gabriele Botta,*** BRTA CIC nanoGUNE, Italy*; M. Knez,* Nanomaterials Senior Scientists Ikerbasque professor in BRTA CIC nanoGUNE, Croatia

We propose an experimental route for locally modifying the magnetic properties of a ALD deposited NiO thin film (paramagnetic) by isothermal gas phase reduction in presence of hydrogen. Continuous NiO films were deposited by alternately pulsing Ni(Cp)2 and ozone at a temperature of 220 °C. In the present work it will be shown that a thin film of Al_2O_3 (5nm), deposited with TMA and ozone as co-precursor, can be used as a mask to prevent the diffusion of the reductant gas (H_2/Ar mixture) in the underlying NiO thin film and suppress its reduction to metallic nickel.

By patterning with eBeam lithography and anisotropic etching the aluminium mask and finely controlling the gas phase reduction step, this method can be utilized to fabricate nanostructured thin films of ferromagnetic domains (Ni) embedded in a paramagnetic medium (NiO).

The optimization of the reduction step will be discussed and the parameters which influence the creation of the magnetic nanostructures will be highlighted. It will be shown that the Al_2O_3 mask thickness and H_2/Ar

pressure, play a crucial role on the diffusion of the gas into the masked areas and how they can be optimized to produce magnetic domains with a high degree of control.

This method will be employed for fabricating two different types of devices for testing the magneto-optical and electronic properties of the ALD materials. The magneto-optical characterization will be carried out by measuring the Magneto Optical Kerr Effect (MOKE) response of nickel nanoarrays produced in different annealing conditions (varying temperature, and reductant pressure). The transport measurement of the ferromagnet will be carried out on a Hall Bar device and the results will be compared with literature demonstrating that this methodology can be used to produce devices with novel functional designs.

AA-TuP-63 Optical and Electrical Device Properties of Plasma-Ald Grown β-Ga_2O_3, *A. Rezk,* Khalifa University of Science, Technology & Research, United Arab Emirates*; I. Saidjafarzoda,* University of Connecticut*; **Ali Kemal Okyay**,* Stanford University*; A. Nayfeh,* Khalifa University of Science, Technology & Research, United Arab Emirates*; N. Bıyıklı,* University of Connecticut

Wide bandgap (WBG) semiconductors, such as GaN and SiC make the backbone of high-power high-frequency electronics. However, production complexity and high-cost of these materials make such technologies less widespread. Gallium oxide (Ga_2O_3) is an emerging WBG semiconductor recently attracting great attention due to its superior electrical properties in this regard. To compete against the mature WBG materials which are grown typically at >1000°C, a substantially lower temperature deposition technique for crystalline Ga_2O_3 is critical, particularly for its integration with temperature-sensitive substrates. In this study Ga_2O_3 films were grown on Si, sapphire, glass, and Kapton substrates via hollow-cathode plasma-assisted atomic layer deposition. Films were deposited using triethylgallium and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 150-240°C substrate temperature and 30-200W rf-power range. Additionally, each unit AB-type ALD-cycle was followed by an *in-situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20sec varied over 50-300W rf-power. X-ray diffraction showed that Ga_2O_3 films grown without *in-situ* plasma annealing exhibited amorphous character irrespective of both substrate temperature and rf-power. Though, with the incorporation of the *in-situ* Ar-annealing step the films grown on Si and glass displayed polycrystalline *β*-Ga_2O_3 crystal phase with further improving crystallinity and film density (from 5.07 to 5.60g/cm^3) with increasing Ar-annealing plasma power. However, XRD analysis of samples deposited at 240°C on sapphire revealed epitaxial monoclinic *β*-Ga_2O_3.

Conductive atomic force microscopy (CAFM) is used to investigate the structural and electrical characteristics of *β*-Ga_2O_3films. CAFM is used to generate the electrical I-V response of the grown films on Si. For the electrical measurements and topography, Au coated AFM tips with a 146 kHz resonance frequency and force constant of 1.2-29N/m are used. The used Asylum Research MFP-3D cAFM utilizes a probe holder (908.036) which is capable of measuring currents from ~1 pA to 20nA. During all electrical measurements the tips were grounded, and a bias was applied to the substrate.

Optical properties of the *β*-Ga_2O_3films were evaluated by building metal-semiconductor-metal photodetectors. The devices were illuminated by UV light (254nm) and photoresponse and dark current behavior were extracted. The reflection and the transmission spectra were measured using a UV–VIS spectrophotometer as a function of the incident wavelength, ranging from 250nm to 1500nm.

AA-TuP-64 The Electrical and Physical Characterization of n-type MoO_x Thin-Film Fabricated by Plasma-Enhanced Atomic Layer Deposition, *D. Wang,* Feng Chia University, Taiwan*; **Pi-Chun Juan**, C. Tou,* Ming Chi University of Technology, Taiwan*; W. Cho, C. Chen, C. Kei,* National Applied Research Laboratories, Taiwan

The MoOX thin films have been successfully fabricated by PE-ALD technique with $Mo(CO)_6$ as the precursor. The physical and electrical properties as functions of film thickness and plasma power are studied. The intensity of crystallization increases with increasing film thickness of MoO_x, while decreases with increasing plasma power. The crystalline belongs to monoclinic b-MoO_3 phase. The transmittance is lower at thicker samples which show more crystallization than thinner films. Similarly, lower intensity of x-ray diffraction patterns at higher plasma power behaves low transmittance, which is corelated to the refractive index. In order to understand the current transportation of oxygen-deficient MoO_x in our case, the Hall measurement equipped with precision pA-level source meters has been performed. We found that MoO_x films prepared are semiconductor n-type conducting materials. The carrier concentration increases with increasing film thickness, but slightly decreases with increasing the plasma power. Though the concentration variation is small by different power, the resistivity shows five times increase as the plasma power changing from 50 W to 150 W. The formation of oxygen vacancies during ALD process, which induce n-type conductivity may play an important role in current behavior. When the thickness of film increases, the amount of oxygen vacancies is expected to be increased, which leads to a lower resistivity. On the other hand, the increase in plasma power, no matter what the carrier concentration or conductivity decreases, which is due to less oxygen vacancies formed in MoO_x with more reaction with oxygen reactant.

AA-TuP-65 Enhanced Self-Assembled Monolayer Surface Coverage by ALD NiO in P-I-N Perovskite Solar Cells, *N. Phung, M. Verheijen, A. Todinova, K. Datta, M. Verhage,* Eindhoven University of Technology, Netherlands*; A. Al-Ashouri, H. Köbler, X. Li, A. Abate, S. Albrecht,* Helmholtz Zentrum Berlin, Germany*; **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Perovskites have attracted tremendous attention due to their excellent opto-electronic properties, enabling perovskite solar cells (PSCs) with a record efficiency of 25.5%[1]. ALD has been used widely in the perovskite field to deposit contact layers, buffer layers, and encapsulation layers. Notably, ALD NiO has been used successfully as hole transport layer (HTL) in PSCs.[2] In this contribution, we further investigate the application of ALD NiO, in combination with self-assembled monolayer (SAM) using MeO-2PACz ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid)in p-i-n PSCs.[3] We fabricate 8 nm ALD NiO to use in PSCs by bis-methylcyclopentadienyl-nickel ($Ni(MeCp)_2$) as precursor and O_2 plasma as co-reactant at a substrate temperature 150°C. Specifically, we focus on the surface coverage of SAM on ALD NiO/ITO and compare with the coverage directly on ITO.[4] Surface coverage is highly relevant in contacts for photovoltaic devices, since non-covered areas can result in electrical shunts, thus reducing the device efficiency.

Herein, we adopt TEM and analyse the ITO/(NiO/)SAM interface. Processing SAM directly on ITO results in an inhomogeneous layer, with areas exhibiting low molecular density. In contrast, the presence of NiO induces a homogenous SAM formation, characterized by a higher optical density (via spectroscopic ellipsometry) compared to ITO/SAM. This improvement of surface coverage is due to a higher hydroxyl group concentration on the NiO surface when compared to ITO, as revealed by XPS. Moreover, conductive AFM mapping reveals exposed ITO areas due to insufficient SAM coverage on ITO. Instead, ITO/NiO/SAM layer exhibits a uniform and low current map indicating a good coverage of SAM on NiO, and conformality of NiO on ITO. This difference in surface coverage translates into different devices efficiency spread when using the layers as HTL in PSCs using $CsFAMAPb(I_{0.83}Br_{0.17})_3$ with FA and MA being formamidinium and methylammonium, respectively. Specifically, a larger efficiency spread with standard deviation of 1.1% is observed for ITO/SAM devices. Instead, the implementation of ALD NiO, by improving the SAM surface coverage, leads to a narrower distribution of efficiency, with a standard deviation down to 0.5%. This study indicates that the bi-layer ALD NiO/SAM can enable highly efficient large area PSCs, which is relevant for upscaling the technology.

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AA-TuP-66 Direct Chemical Vapour Deposition of Graphene on Atomic Layer Deposited Functional Nickel Oxide, ***Geedhika Poduval**, D. Ji, S. Bremner, R. Joshi, B. Hoex,* UNSW Sydney, Australia

The rise of graphene-based devices has generated enormous scientific attention to directly synthesize high-quality graphene onto insulating substrates. Currently, graphene layers are synthesized by chemical vapour deposition (CVD) at high temperatures on transition metals Cu and Ni. The graphene layer is subsequently transferred to the desired substrates for device applications. Conventionally, the transfer process involves a solution-based approach, which results in its chemical and physical denaturing. The transferability and quality of the graphene layer significantly influence the final device performance, meaning device yield remains a significant challenge.

Here, a new method is reported to directly synthesize graphene films on a functional layer - NiO_x without the need for an additional metal catalyst. In contrast to the conventional approach, where hazardous gases methane and hydrogen are used, here, ethanol, a non-toxic, liquid precursor, is used to directly grow graphene on atomic layer deposited (ALD) NiO_x. The first successful graphene growth is demonstrated, and its growth mechanism is investigated in detail. The reduction of the surface atomic layers of NiO_x to metallic Ni is found to be key to catalyzing graphene growth. This process resulted in bilayer graphene flakes. Further, the impact of physical vapour deposited (PVD) NiO_x and varying NiO_x thickness on graphene growth is studied. It is found that the PVD NiO_x layer is completely reduced during the CVD process. Whereas the dense layers afforded by ALD seem to be required to limit the reduction of the metal oxide film to the top surface resulting in the preservation of the metal oxide film at the substrate. The capability to directly grow graphene on a functional oxide layer that also acts as the catalyst using a nontoxic liquid precursor enables seamless integration of graphene into next-generation solar cells and optoelectronic devices.

AA-TuP-67 The Role of Defects in Tuning the Properties of Highly Conductive Cuprous Oxide Thin Films Revealed Through Positron Annihilation Spectroscopy, ***Abderrahime Sekkat***, LMGP/IMEP-LAHC/SIMAP, France; *M. Oskar Liedke,* HZDR, Germany; *V. Huong Nguyen,* Phenikaa, Viet Nam; *M. Butterling,* HZDR, Germany; *F. Baiutti, J. de Dios Sirvent,* IREC, Spain; *M. Weber, L. Rapenne, D. Bellet,* LMGP, France; *G. Chichignoud,* SIMAP, Grenoble-INP, CNRS, France; *A. Kaminski-Cachopo,* IMEP-LAHC, France; *E. Hirschmann, A. Wagner,* HZDR, Germany; *D. Muñoz-Rojas,* LMGP, France

Cu_2O, being a non-toxic and abundant p-type semiconductor, is drawing a lot of attention for several energy applications. So far, the lowest resistivity values have been obtained for films deposited by physical methods and/or at high temperatures (~1000 °C), limiting their mass integration. In this work, Cu_2O thin films with record resistivity values of 0.4 Ω.cm were deposited at only 260 °C by atmospheric pressure spatial atomic layer deposition, a scalable chemical approach. The carrier concentration (7.10^{14}-2.10^{18} cm^{-3}), mobility (1- 86 cm^2/V.s), and optical bandgap (2.2-2.48 eV) can be simply tuned by varying the deposition parameters. Our results show that the transport properties of the films are correlated to the nature and concentration of defects, as revealed by positron annihilation spectroscopy (PAS) studies and density functional theory calculations. This study reveals the existence of large complex defects and the evolution of the overall defects concentration and transport properties evolving with varying deposition conditions, opening prospects for the adoption of Cu_2O.

AA-TuP-68 Highly Conformal CoO_X Layer Formed by Atomic Layer Deposition for High Performance Supercapacitors, *S. Adhikari, G. Noh,* Chonnam National University, Korea (Republic of); ***do heyoung kim,*** 5-404, Engineering Building 5,, Korea (Republic of)

Binary metal sulfides (BMSs) have attracted great attention over the decades for electrochemical energy storage systems. In particular, BMSs acts as a promising electrode material for supercapacitor application. Compared to their individual sulfide counterparts, BMSs exhibit enhanced electronic conductivity with faster redox reactions. However, stability and capacity retention are the bottlenecks that restricts their applicability. In this regard, atomic layer deposition (ALD) has emerged as an advanced deposition technique, which can tune the performance through atomic level conformal deposition contributing in stable surface reactions for prolonged time-period. In addition, the specific capacitance is influenced by the ALD thickness, leaving more room to understand the electrode-electrolyte interactions. Therefore, the present work will demonstrate the supercapacitor performance of ALD CoO_x on hydrothermally grown and sulfurized $MnCo\text{-}_2S_4$ nanoneedles. The effect of ALD thickness on performance, stability, and capacity retention will be understood and evaluated.

AA-TuP-69 Ultra-low Resistivity Molybdenum Carbide Thin Films Deposited by Plasma-Enhanced Atomic Layer Deposition Using a Cyclopentadienyl-based Precursor, ***Min-Ji Ha***, *J. Choi, J. Ahn,* Hanyang University, Korea (Republic of)

As memory devices become ultra-miniaturized, the increase in the resistance of the metal line due to the decrease in the line width has become a very critical issue. Mo-based materials have been studied as candidates for next-generation metal line materials because of their low resistivity at low thickness and excellent oxidation resistance. However, the development of precursors suitable for vapor deposition methods (such as atomic layer deposition) is immature. In this study, we propose an ultra-low resistivity MoC_x thin film using a cyclopentadienyl-basedprecursor as a new metal line candidate. Using a halogen-free liquid precursor, MoC_x thin films were successfully deposited by PEALD in a wide process window of 200-300 ºC. We confirmed that uniform and continuous films were deposited on the SiO_2 substrates without any significant incubation period. The most important result of this study is that as-deposited MoC_x thin films exhibited an ultra-low resistivity of 8-20 μΩ·cm,and such ultra-low resistivity was maintained even with a thickness as thin as 4.25 nm and after rapid thermal annealing up to 600 ºC. This is the lowest resistivity value of reported metal line candidate materials available at the sub-10 nm device scale level. The ultra-low resistivity at a very thin thickness and excellent thermal stability suggest the possibility that the MoC_x thin films proposed in this study can be applied in various applications as a next-generation metal line material in the semiconductor industry.

AA-TuP-70 A Simple Strategy to Realize Super Stable Ferroelectric Capacitor via Interface Engineering, ***Hyo-Bae Kim,*** Hanyang University, Korea (Republic of); *K. Dae, J. Jang,* Korea Basic Science Institute (KBSI), Korea (Republic of); *J. Ahn,* Hanyang University, Korea (Republic of)

Fluorite-structure ferroelectric thin films have been extensively studied as promising candidates for next generation non-volatile memory. However, these ferroelectric thin films have fatal issues such as low cycling endurance, and wake-up and fatigue during cycling endurance tests. These problems are reportedly caused by oxygen vacancies, which form due to the interface reaction between the thin films and bottom electrode during deposition and the post-annealing process. Therefore, we expected that the critical problems of fluorite-structure ferroelectric thin films can be solved by controlling the amount of oxygen vacancies by preventing unwanted interface reactions. In this work, the enhanced ferroelectric characteristics of $Hf_{1-x}Zr_xO_2$ thin films that control the oxygen vacancies in thin films through interfacial pre-treatment were investigated. Interfacial pre-treatment using an oxygen source can reduce oxygen vacancies and improve crystallinity through intentional oxidation of the bottom electrode. As a result, the remanent polarization value was increased by about 1.6 times by applying the optimized pre-treatment condition, and the measured $2P_r$ value of 73 μC/cm^2. Furthermore, it exhibited very stable ferroelectric properties without a wake-up effect or significant fatigue, up to 10^8 cycles even under a severe electric-field of 3.5 MV/cm. This simple strategy provides a new avenue to effectively improve the performance and cycling endurance of devices with ferroelectric thin films.

AA-TuP-71 Area-Selective Atomic Layer Deposition Brings Plasmonic Biosensors Into the Electronic Age, ***Corbin Feit,*** University of Central Florida; *P. Rathi, S. Singamaneni,* Washington University in St. Louis; *P. Banerjee,* University of Central Florida

Label-free biosensing platforms based on refractive index sensitivity of localized surface plasmon resonance (LSPR) hold significant importance in healthcare as diagnostic tools. Colorimetric biosensors use plasmonic nanostructures that exhibit significant light-matter enhancement in the nanoscale. Upon a specific biomarker binding event, optical shifts of the LSPR are detected through spectrophotometry. Point-of-care is limited by the bulky, expensive, and labor-intensive use of spectrometers. Efforts to miniaturize instrumentation diminishes the spectral resolution, which in turn compromises the limit of detection for shifts of the LSPR.

To overcome the limitations that arise from current state-of-art optical readout technologies, we present detailed results of a “plasmo-resistor" sensor that electronically monitors the photocurrent generated by hot electrons (HE) emitted from plasmonic gold nanorods (AuNRs). Nanoscale engineering is required to deposit conductive films for transferring hot electrons through a vicinal medium, while maintaining viable plasmonic nanostructures for conjugation with biomarkers. Area-selective atomic layer deposition (AS-ALD) remains the only suitable technique capable of meeting this constraint. The fabrication and viability of partially embedded AuNRs in AS-ALD of zinc oxide (ZnO) on a two-electrode device is probed by UV-Vis and Raman spectrometry, AFM, and TEM. We investigate the electronic properties of the AuNR-ZnO nanocomposite and demonstrate the excitation of HE mirrors the optical response of the LSPR. Through coupled Raman microspectroscopy and laser beam induced current (LBIC) measurements a change in photocurrent caused by shifts in the LSPR is linked to an aminothiolphenol binding event. This proof-of-concept plasmo-resistor device is expected to pave the way for detection of biomarkers via the coupling of highly sensitive changes to LSPR to an electronic signal thus, negating the use of expensive, bulky and labor-intensive instrumentation.

AA-TuP-73 Annealed ALD TiN_X Layers for Through-Silicon Superconducting Interconnects*, **Kestutis Grigoras,** P. Eskelinen,* VTT Technical Research Centre of Finland, Ltd, Finland*; M. Caputo,* VTT Technical Research Centre of Finlandt, Ltd, Finland*; D. Datta,* VTT Technical Research Centre of Finland, LTD, Finland*; A. Ronzani,* VTT Technical Research Centre of Finland, Ltd, Finland*; E. Mannila, J. Govenius,* VTT Technical Research Centre of Finland, LTD, Finland

The unique mechanical, electrical, and chemical properties of titanium nitride facilitate a wide range of applications. TiN layers are employed as drill coating materials, as MOSFET gate electrodes, as diffusion barriers for Cu, as 3D interconnects, and even as gold imitating coatings on watches. Many of those applications can benefit from atomic layer deposition (ALD), which offers conformal coating and precise control of film thickness [1, 2]. During subsequent fabrication steps, or during device operation, the TiN coating can experience thermal cycling. Therefore, understanding the effect of annealing TiN layers at various temperatures is important.

In this work, we investigate the influence of annealing on electrical conductivity, residual stress, and optical properties of TiN_x layers. Layers are grown on 6-inch wafers by a thermal ALD process at 450ºC using $TiCl_4$ and ammonia as precursors and nitrogen as a carrier gas. Pulse and purge times were tuned in order to change film stress and resistivity. The obtained thicknesses are 50 to 150 nm, and the growth per cycle is approximately 0.19 Å. Coated wafers are annealed for 5 to 10 minutes at 700, 800 or 900ºC in nitrogen atmosphere. As grown and annealed samples are characterized by scanning electron microscope (SEM), 4-point probe measurements, ellipsometry, X-ray diffraction (XRD), and laser reflection based residual stress measurement.

We obtain resistivities of approximately 200 to 300 µOhm cm and tensile stresses of approximately 1.5 GPa for as deposited layers. Tests show that TiN films are sensitive to annealing conditions: presence of humidity or oxygen results in degradation: resistivity increases to the MOhm-cm range, also visually layers change and partly peel off from the substrate (Fig. 1). Minimizing pressure and increasing nitrogen flow during annealing results in uniform and bright films, even for different initial thicknesses (Fig.1). The resistivity also decreases, by a factor of 2 to 3 for layers annealed at 900ºC. This may be explained partly by a change in crystallinity (Fig. 2) and by possible additional nitridation of layers: our earlier investigations by ToF ERDA showed that the main impurity of as grown layers was oxygen [3]. An important result is the increase of the critical temperature of the superconducting phase T_c from 100 mK to 3 K after annealing.

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AA-TuP-74 Plasma-Enhanced Atomic Layer Deposition of Crystalline NiO Films Using Nickelocene and O2 Plasmas for BEOL p-Channel Devices*, S. Ilhom, A. Mohammad, M. Niemiec, D. Zacharzewski, P. Chardavoyne, S. Abdari, **Necmi Biyikli,*** University of Connecticut

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

In an attempt to enhance the hole transport properties in low-temperature as-grown NiO layers, in this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si and glass substrates using nickelocene ($NiCp_2$) and O_2/Ar plasma mixture in two separate plasma reactors equipped with inductively coupled and hollow-cathode plasma sources. Detailed saturation studies using in-situ ellipsometer monitoring were carried out in the HCP-ALD reactor, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms NiCp2 pulse / 5 s purge / 10 s O_2-plasma@ 100W / 5 s purge. To check the growth linearity and obtain thicker films for materials characterization, 800 cycle runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties. The last growth parameter studied was the plasma gas composition, where several O_2/Ar mixtures (20/0, 20/20, 20/50, 50/20 sccm) were tested at the optimal substrate temperature.

The resulting NiO films are characterized for their optical, structural, and electrical properties. Film grown at optimal conditions exhibit refractive index values within a range of 2.1 - 2.2, which is in good agreement with reported values in the literature. NiO films deposited on both Si and glass substrates exhibit polycrystalline single-phase cubic structure (c-NiO). Initial electrical measurements confirm p-type conductivity of the as-grown NiO layers on glass substrates, with resistivity values about 40 and 150 ohm-cm for HCP and ICP samples, respectively. Hall measurements will be carried out, analyzed, and presented in detail as well.

ALD Applications
Room Baekeland - Session AA1-WeM2
ALD for Optical Applications

Moderators: Parag Banerjee, University of Central Florida, Matti Putkonen, University of Helsinki

10:45am **AA1-WeM2-1 Atomic Layer Deposition of Perovskite $K(Ta_x,Nb_{1-x})O_3$ films on Silicon for Integrated Photonics via KOtBu and H_2O**, ***Eric Martin,*** Ohio State University*; J. Bickford,* Army Research Laboratory*; H. Sønsteby,* University of Oslo, Norway*; R. Hoffman,* Army Research Laboratory*; R. Reano,* Ohio State University

Photonic integrated circuits (PICs) have advanced significantly over the last decade with a view towards applications in communications, sensing, and computing in the classical and quantum domains.The fabrication of silicon PICs in particular has transitioned from university cleanrooms to foundry supported process design kits by leveraging mature fabrication techniques from the microelectronics industry.The silicon material system exhibits optical properties that are enabling for compact PICs, such as high index contrast and low optical propagation loss at telecommunications wavelengths, allowing for the demonstration of low power nonlinear optical devices in waveguides based on third order susceptibility.An approach to advance the state-of-the-art performance of nonlinear optics in silicon PICs is to pursue heterogeneous integration. A promising material for this purpose is potassium tantalate niobate (KTN).KTN is a solid solution of $KTaO_3$ and $KNbO_3$ perovskites with a Curie temperature (T_c) that is defined by the Ta:Nb ratio.Bulk KTN crystals show record high Kerr nonlinearity when thermally tuned near T_c.KTN thin films can be grown with controllable Ta:Nb ratios via atomic layer deposition (ALD) using potassium tert-butoxide (KOtBu), tantalum ethoxide ($Ta(OEt)_5$), niobium ethoxide ($Nb(OEt)_5$) and H_2O precursors.To date, deposition of KTN films on silicon substrates has not been reported.In this work, we explore several approaches for obtaining perovskite $KTaO_3$ and KTN thin films on silicon using KOtBu, $Ta(OEt)_5$, $Nb(OEt)_5$, and H_2O precursors. Our approaches include varying the ALD process parameters for the metalorganic and H_2O co-precursors, chemically modifying the substrate surface, deposition of interfacial layers, and implementing ALD equipment modifications.We report the K uptake as a function of ALD process parameters using both refractive index obtained from spectroscopic ellipsometry and quantification from X-ray photoelectron spectroscopy (XPS).For a subset of samples, we report the crystal structure of our RTA annealed ALD films using X-ray diffraction (XRD). For the first time, we demonstrate perovskite $KTaO_3$ and KTN films on silicon by ALD.

11:00am **AA1-WeM2-2 Low-temperature ALD Sb_2Te_3 for Self-powered Broad-band Photodetector**, ***Jun Yang****, A. Bahrami, S. Mukherjee, S. He, S. Lehmann, K. Nielsch,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science Dresden, Germany

P-type Sb_2Te_3 thin film was deposited by atomic layer deposition (ALD) at 80 °C using $(Et_3Si)_2Te$ and $SbCl_3$ as precursors. The good crystal quality, low defect, and excellent uniformity of low-temperature ALD processed Sb_2Te_3 was supported by Raman, transmission electron microscopy, and XPS. Furthermore, high performance self-powered broad-band photodetectors based on Sb_2Te_3/Si heterostructure were fabricated. The photodetector has a wide detection range of 405 to 1550 nm. Meanwhile, a high responsivity of 4287 mA/W at 405 nm, and a quick response speed of 98 µs (t_{rise}) were obtained under 0 bias voltage, which could be ascribed to the strong built in electric field between p-type Sb_2Te_3 thin film and n-type Si. The temperature dependent performance of Sb_2Te_3/Si photodetector was thoroughly examined. Resistivity, conductivity, and carrier concentration of Sb_2Te_3 were carried out at temperature ranging from 273 K to 473 K to reveal intrinsic mechanism. The Sb_2Te_3/Si heterostructure self-powered photodetector with excellent performance based on ALD process shows the great potential application in optoelectronic devices.

11:15am **AA1-WeM2-3 Preparation of High Mobility Indium Hydroxide Doped by Atomic Layer Deposition and Study on Photoelectric Properties**, ***Liangge Xu,*** Harbin Institute of Technology, China

At present, the industrialization of metal mesh and tin doped indium oxide (ITO) film cannot meet the high transmittance requirements of infrared band. Therefore, how to achieve high carrier mobility has become a hot topic. In order to solve the above problems, In_2O_3:H film is selected, which is a special transparent conductive oxide film. On the one hand, hydrogen has a very small volume and mass, and will not produce impurity scattering in the process of electron transport; On the other hand, hydrogen is distributed in the gap of the indium oxide lattice, resulting in almost no lattice distortion, so it does not increase the number of grain boundaries and reduce the grain boundary scattering. The combined effect of these two factors makes the hydrogen doped indium oxide (In_2O_3:H) thin films have high carrier mobility, which can achieve high infrared transmittance by reducing the carrier concentration on the basis of ensuring the electrical properties.

In this paper, the growth rate, microstructure and photoelectric properties of In2O3:H films were investigated by changing the deposition process parameters. When the deposition temperature is 100 ℃, incomplete reaction occurs during deposition, and the growth rate is slow. The film is amorphous. At this time, the carrier mobility is low, which is only 30.18 cm^2/Vs, and the optical properties are good, the transmittance can reach 80% at 4 μm; With the increase of deposition temperature, the growth rate gradually stabilized at 0.1nm/cycle, the amorphous state gradually changed to crystalline state, the carrier mobility increased sharply, and the highest was 64.05 cm^2/Vs, and the carrier concentration and the optical properties decreased. The ratio of deposition time of InCp / (O_2 + H_2O) and the reaction time of InCp have little effect on the electrical and optical properties. With the increase of deposition period, the carrier mobility can reach up to 80 cm^2/Vs, but the optical performance is very poor, the transmission rate at 4 μm is only 39.5%.

11:30am **AA1-WeM2-4 ALD MgF2 Using $(EtCp)_2Mg$ and SF_6 Remote Plasma Source**, ***Hoon Kim****, . Huang, . Allen, E. Pierce, , J. Wang,* Corning Inc.

Magnesium fluoride (MgF2) is a key material for Deep Ultra-Violet (DUV) and Far UV optics due to its wide bandgap and high resistance of oxidation. ALD process enables conformal coatings and precise thickness control on 3D shape optics. ALD MgF2 has been demonstrated using anhydrous hydrogen fluoride (HF) as fluorine source. However high concentration HF has safety concern in handling and residue in the reactor. Thus, safer fluorine source should be considered for industrial use. Hhfac has also been evaluated, but it requires O3 to activate the fluorine which results in oxygen and carbon incorporation in the film. The impurities are an absorption source for the UV range. SF6 is evaluated as fluorine source for AlF3, but no report for MgF2. In this study, we demonstrated the MgF2 ALD using SF6 remote plasma. The growth rate, impurity level and conformality were evaluated. Optical properties such as dispersion and transmittance were obtained. Hot wall batch reactor with remote plasma source was employed in this study. Fluorine radical was generated by using SF6 flow through Inducted coupled plasma (ICP) source. (EtCp) 2Mg was used as precursor. A prism shape surrogate was used to evaluate coverage on 3D shape. Thickness and reflectance were measured by an ellipsometer. Impurity of the film was measured by XPS and SIMS. Direct reduction of the precursor using SF6 plasma caused high carbon incorporation in the film due to the reaction of Cp ligand and fluorine. XPS results showed that CFx bonds are detected in the film. To address this issue, reducing agent to remove the Cp ligand from adsorbed precursor was introduced before SF6 exposure. This approach effectively removes the carbon incorporation and forms high purity MgF2 film. This ALD film has lower impurity level than that of in-house PVD MgF2. The growth rate of ALD MgF2 is 0.4Å/cycle at 150oC. The refractive index at 550nm is 1.33 which is same as inhouse PVD MgF2. The deposited film is polycrystalline. Other optical properties will be reported.

11:45am **AA1-WeM2-5 Moisture Sensitivity of ALD Metal Fluorides for Far UV Optical Coatings**, ***Robin Rodríguez****, J. Hennessy, A. Jewell, S. Nikzad,* Jet Propulsion Laboratory (NASA/JPL)

We report on the use of atomic layer deposition (ALD) for the development of metal fluoride thin films relevant to optical coatings operating at far ultraviolet wavelengths (FUV, 90-200 nm). The use of metal fluoride materials like MgF_2, AlF_3, LiF, CaF_2, and LaF_3 is relevant to all FUV optical systems for applications like anti-reflection coatings, dichroic beam splitters, bandpass filters, and reflective mirror coatings. However, many metal fluorides have associated concerns with environmental stability, primarily related to water vapor exposure. For example, LiF-protected aluminum mirror coatings can experience reflectance-losses if stored in modest relative humidity environments (RH ~40%). Initial space-based demonstrations of ALD coatings have shown improved stability by depositing a thin 1–2 nm capping layer of MgF_2 or AlF_3 onto the LiF-protected mirrors. In this work, we have conducted a broader study of the moisture sensitivity of ALD materials. This includes physical vapor deposition (PVD) of AlF_3 mirror coatings capped with ALD MgF_2 layers on Si, as well as stand-alone ALD coatings of MgF_2, AlF_3, CaF_2, and LiF on Si

subjected to both long-duration and accelerated aging tests and then characterized by FUV reflectance measurements, spectroscopic ellipsometry, atomic force microscopy, x-ray photoelectron spectroscopy, x-ray diffraction, and secondary-ion mass spectrometry. To the best of our knowledge, this work also reports the first instance of CaF_2 and LaF_3 coatings deposited by ALD using anhydrous HF.

The observed changes in optical properties, surface morphology, and film composition can provide guidelines on storage conditions for these materials for future space instrumentation, and serves as a baseline for the direct comparison of material produced by PVD versus ALD.Finally, we also describe a new test reactor used in the work above that has enabled the deposition of PVD aluminum mirror coatings and ALD metal fluorides within the same vacuum chamber, to prevent oxidation of the aluminum surface and minimizing the time between metal evaporation and ALD encapsulation.

ALD Applications
Room Van Rysselberghe - Session AA2-WeM2
ALD for Memory Applications I

Moderators: Robert Clark, TEL Technology Center, America, LLC, Charles Dezelah, ASM

10:45am **AA2-WeM2-1 Sub 10-nm Ferroelectric HfO_2 Capacitors Doped with Gd***, **Evgeniy Skopin**, N. Guillaume, L. Alrifai, A. Bsiesy,* LTM - MINATEC - CEA/LETI, France

Recent discoveries of the ferroelectric properties of doped HfO_2 opens the possibilities of its integration in Ferroelectric-based non-volatile Random-Access Memories (FeRAMs). Replacing memories based on perovskites materials by ferroelectric HfO_2 has many decisive advantages. Indeed, HfO_2 is readily used in CMOS back end of the line, and its use opens the possibility to grow thinner layers of around 10 nm *vs* 70-100 nm for the conventional ferroelectric perovskites. Thinner layers are mandatory for integration in advanced sub 100 nm CMOS technology nodes.

Plasma Enhanced Atomic Layer Deposition (PEALD) allows the synthesis of a different range of materials such as oxides and metals with low surface roughness and precise thickness control. TiN metal (M) layers and Gd doped HfO_2 insulator (I) layer were grown in the same PEALD chamber without contact with the air between depositions to synthesize ferroelectric MIM capacitors. Changing ratios between Hf and Gd PEALD cycles inside one supercycle allows choosing an appropriate Gd doping concentration. In its order, during annealing, Gd doping in HfO_2 (Gd:HfO_2) leads to a crystallization of HfO_2 in a metastable non-centrosymmetric orthorhombic phase, which induces the HfO_2 ferroelectric properties. A decrease of the ferroelectric oxide thickness can allow operating lower switching voltages for the low power circuits.

Continuing our previous work [SB], by using the growth of MIM capacitor by PEALD in one batch (*i.e*. without air break between metal, insulator, and metal layers), we recently demonstrated the ferroelectricity of sub-10 Gd:HfO_2 layers (8.8nm-, 6.6nm, and 4.4nm-thick layers) in TiN / Gd:HfO_2 / TiN stacks and studied the remnant polarization amplitude change with the Gd:HfO_2 layer thickness. Structural measurements (X-ray diffraction and reflectometry) confirmed a HfO_2 transformation to the orthorhombic (ferroelectric) phase. Electrical measurements showed that switching voltage can be decreased for the thinner Gd:HfO_2 layers (hysteresis loop measurements and Positive Up Negative Down measurements). Polarization switching cycling measurements demonstrate ferroelectric endurance of at least up to 10^8 cycles. This work opens the possibilities for the integration of sub-10nm Gd:HfO_2 in the memory device circuits thanks to the unique PEALD deposition capabilities.

References:

[SB] Applied Physics Letters 117.25 (2020): 252903.

11:00am **AA2-WeM2-2 Controlling Stochastic Resistive Switching in Organic-Inorganic Hybrid Memristor by Vapor-Phase Infiltration***, A. Subramanian,* Stony Brook University*; N. Tiwale, K. Kisslinger, **Chang-Yong Nam**,* Brookhaven National Laboratory

Resistive random-access memory (RRAM) is promising for next-generation data storage and non-von Neumann computing hardware. However, tuning device switching characteristics and, particularly, controlling their stochastic variation remain as critical challenges. Here, we report new organic-inorganic hybrid RRAM media whose bipolar switching characteristics and stochasticity can be controlled by vapor-phase infiltration (VPI), an ex-situ organic-inorganic hybridization technique derived from atomic layer deposition (ALD). Hybrid RRAMs based on AlO_x-infiltrated SU-8 doped with sliver perchlorate feature facile tunability of device switching voltages, off-state current, and on-off ratio by adjusting the amount of infiltrated AlO_x in the hybrid, wherein molecular network of AlO_x is homogenously distributed through the polymer free volume by the sequential infiltration of trimethylaluminum (TMA) and water vapor. Furthermore, a significant reduction in the stochastic, cycle-to-cycle variations of switching parameters, such as off-state current and set/reset voltages, was enabled by AlO_x infiltration, driven by the infiltration-induced changes in mechanical, dielectric, and chemical properties of the organic medium and their influence on the dimension and formation characteristics of a conductive silver filament. Finally, we demonstrate multi-level analog switching, potentially useful for neuromorphic applications, by controlling switching compliance current, as well as direct, one-step device patterning ability exploiting the negative-tone resist feature of SU-8. With the demonstrated control over switching characteristics and stochastic variation, combined with analog switching and one-step patterning capabilities, the results not only present a novel hybrid medium for RRAM applications but also showcase the utility of VPI for developing new, high-performance hybrid RRAM devices based on photoresist materials.

11:15am **AA2-WeM2-3 Atomic Layer Deposited Vanadium Oxide Thin Films for Thermocromic and Microelectronic Applications***, **Zsofia Baji**, J. Volk, L. Pósa, G. Molnár,* Centre for Energy Research, Hungary*; A. Surca, G. Drazic,* National Institute of Chemistry, Slovenia

Vanadium oxides are much-researched materials due to their wide range of applications from microelectronics, smart electrochromic and thermochromic windows, metamaterials, gas sensors, programmable critical thermal sensors to battery energy storage. V_2O_5 has been the most widely examined for energy storage and electrochromism, as the Li ions can easily be intercalated between its atomic layers. On the other hand, VO_2 undergoes a reversible transition at 68°C, where a change in light and electrical conductivity occurs, therefore, VO_2 is widely researched as a promising material for resistive switching and thermochromism. Resistive switching is presently at the core of emerging technologies, such as memristors and neuromorphic computing. By the switching between the insulating and metallic phase of VO_2, the switching of signals for nanoelectronical applications becomes possible. Alternative switching mechanisms are also widely researched, such as the field-induced transition. An advantage of the ALD method in the preparation of these films would be the control of the deposition parameters and an easy doping, which allows a better control of material properties (crystallinity, stoichiometry and defects), and, thus, the transition temperature.

The atomic layer deposition of vanadium oxides has been in the focus of much research effort. Several precursors and different reactions can be used for this purpose, but there are some substantial difficulties with all of them. Vanadium oxy-tri-isopropoxide, Tetrakis ethylmethyl-amino vanadium (TEMAV) or VCl_4 are all promising candidates for the process.

Most reports on the ALD of vanadium-oxides present the preparation of V_2O_5 which is the more stable phase and is easier to deposit. An advantage of the ALD method is that the oxidation state of the deposited films can be tuned by the selection of the reactant. More oxidising reagents (e.g. oxygen plasma) will result in films with higher oxidation states, while reactions with hydrogen or ammonia plasma yield lower oxidation states. In this way, by choosing the appropriate reactants and deposition parameters the preparation of VO_2 can be achieved.

The present work examined the ALD process of TEMAV and different oxidants (water, oxygen plasma) a number of annealing procedures in oxidising and reducing atmospheres. The films were annealed to improve the crystallinity and stoichiometry. Their properties were examined with Raman spectroscopy and transmission electron microscopy. The switching properties were analysed electrically and optically, and test structures were demonstrated.

11:30am **AA2-WeM2-4 Brain-Based Inspiration: Towards Neuromorphic Computing With ALD Based Memristive Devices***, E. Perez, M. Kalishettyhalli Mahadevaiah, E. Perez-Bosch Quesada,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany*; T. Rizzi,* IHP - Leibniz-Institut fuer innovative Mikroelektronik, Germany*; **Christian Wenger**,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany **INVITED**

Due to its advantages of massive parallelism, high energy efficiency, and cognitive functions, brain-inspired neuromorphic computing is attracting immense interest. As the basic unit cell for learning algorithms, the

implementation of synaptic behavior into memristive devices is the key step toward neuromorphic computing.

Recent advances in the performance of resistive random access memory (RRAM) acting as memristive devices have led to a significant interest in neuromorphic applications. Although RRAM based memory arrays demonstrated excellent performance parameters, the variability is still a critical issue. Controlling this intrinsic phenomenon requires employing program-verify schemes. In this talk, an optimized scheme to minimize resistance state dispersion and to achieve reliable multi-bit operation is evaluated.

However, statistical variations can be tolerated in computing applications like neuromorphic networks. The synaptic behavior memristive devices can be evaluated by applying successive algorithms consisting of set or reset pulses. These algorithms can be used to study the synaptic functionality of memristive arrays.

Nevertheless, there is still a huge gap between the physical implementation and the verification of circuits and systems proposed for memristive devices. The first step, required to fill the gap, is the development of analog simulation tools, which are the base for the successful implementation of digital CMOS circuits with memristive elements. New designs and concepts need to be supported up by physical implementation and verification to be reliable. That means, new simulation tools for memristive devices have to address the following issues: device variability, cycling variability, data endurance, data retention as well as device switching speed. Meaning that memristive device models still have a long way to be completed.

ALD Applications
Room Van Rysselberghe - Session AA1-WeA
ALD for Memory Applications II

Moderators: Noureddine Adjeroud, Luxembourg Institute of Science and Technology (LIST), , Christian Wenger, IHP - Leibniz Institut fuer innovative Mikroelektronik

1:30pm **AA1-WeA-1 Effects of Ultra-thin Atomic Layer Deposited MgO Buffer Layer on Structural and Electrical Properties of Beo and HfO_2 Films for Dynamic Random Access Memory Capacitors**, ***Bo Wen Wang**, H. Song, S. Byun, D. Kwon, J. Lim, H. Seo, T. Kim, H. Paik, J. Shin, C. Hwang,* Seoul National University, Korea (Republic of)

In this work, magnesium oxide (MgO) thin films were grown via atomic layer deposition (ALD) as a buffer layer on titanium nitride (TiN) bottom electrode using bis(cyclopentadienyl) magnesium as the Mg precursor. Subsequently, beryllium oxide (BeO) and hafnium oxide (HfO_2) films were deposited by ALD on top of the MgO buffer layer using diethyl beryllium, tetrakis(ethylmethylamino) hafnium as the Be and Hf precursors, respectively. O_3 was used as the oxygen source for each ALD process. Such stacked films (MgO/BeO, MgO/HfO_2) were used as insulator layers for metal-insulator-metal (MIM) devices with TiN as bottom and top electrodes. The leakage current density (J) levels of the MIMs were significantly suppressed when the MgO buffer layer with a thickness of only ~1 nm was adopted. As a result, the 1 nm MgO buffer layer enabled a smaller total equivalent oxide thickness (EOT) value (defined by $J < 1\times10^{-7}$ A cm^{-2} at an applied voltage of + 0.8 V) for the application of dynamic random access memory capacitor. The electrical performance improvement might be caused by the structural change with the addition of the MgO buffer layer. Therefore, the possible templating effect of in-situ crystallization of ultra-thin (< ~ 3nm) BeO and HfO_2 films on the MgO buffer layer, which was improbable directly on TiN, was investigated through scanning/transmission electron microscopy (S/TEM). Moreover, the intermixing occurring during deposition and post-deposition annealing were discussed based on the depth profiles by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

1:45pm **AA1-WeA-2 Comparison of TiO_xN_{1-x} Layer Formation at Ferroelectric-$Hf_xZr_{1-x}O_2$/TiN Interface by H_2O and O_2 Plasma Gases During Atomic Layer Deposition**, ***Takashi Onaya**,* National Institute of Advanced Industrial Science and Technology/Research fellow of Japan Society for the Promotion of Science, Japan*; T. Nabatame, T. Nagata, S. Ueda,* National Institute for Materials Science, Japan*; Y. Jung, H. Hernandez-Arriaga, J. Mohan, J. Kim,* The University of Texas at Dallas*; C. Nam, E. Tsai,* Brookhaven National Laboratory*; H. Ota, Y. Morita,* National Institute of Advanced Industrial Science and Technology, Japan

The discovery of the ferroelectricity in HfO_2-based films offered the possibility for the integration and scalability of ferroelectric memory devices because of capability of atomic layer deposition (ALD) technique. In our previous study, we have reported that the $Hf_xZr_{1-x}O_2$ (HZO) films fabricated by plasma-enhanced ALD (PE-ALD) using O_2 plasma showed a higher remanent polarization ($2P_r$) and superior fatigue properties compared to those fabricated by thermal ALD (TH-ALD) using H_2O gas. [1] To clarify the cause of these differences in ferroelectricity, we focused on the interface between the HZO film and TiN bottom-electrode (BE-TiN). In this work, we studied the TiO_xN_{1-x} interfacial layer (IL) formation between BE-TiN and HZO film deposited by TH- and PE-ALD and the ferroelectricity of TiN/HZO/TiN capacitors.

TiN/HZO/TiN capacitors were fabricated as follows: A 10-nm-thick HZO film was deposited on BE-TiN by TH- and PE-ALD at 300°Cusing H_2O and O_2 plasma as oxidants, respectively, and a (Hf/Zr)[N(C_2H_5)CH_3]$_4$ (Hf:Zr = 1:1) cocktail precursor. The Hf/Zr ratios in TH- and PE-ALD films were 0.4/0.6. Next, post-deposition annealing (PDA) was performed at 400°C for 1 min in a N_2 atmosphere. Finally, TiN top-electrode was fabricated by DC sputtering. The crystallinity was analyzed using synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) at the NSLS Ⅱ, Brookhaven National Laboratory. A TiO_xN_{1-x} IL formation was evaluated by synchrotron hard X-ray photoelectron spectroscopy (HAXPES) at the BL15XU of SPring-8.

The PE-ALD film dominantly formed ferroelectric orthorhombic phase evaluated by GIWAXS, resulting in a higher $2P_r$ of 20 μC/cm^2 than that of the TH-ALD film (13 μC/cm^2).Compared with the maximum $2P_r$ after wake-up field cycling, the PE-ALD film showed less $2P_r$ degradation (~33%) after 10^6 cycles, while the $2P_r$ of TH-ALD film decreased by ~47%. These superior fatigue properties of the PE-ALD film were attributed to the formation of TiO_xN_y IL between the HZO film and BE-TiN during the ALD process, which can prevent the formation of oxygen vacancies in the HZO film during the PDA process and field cycling, evaluated by HAXPES spectra for Ti 2p and N 1s. Based on these results, we found that the TiO_xN_y IL formation at the TiN/HZO interface using O_2 plasma during the ALD process plays an important role to stabilize the redox reaction and achieve superior fatigue properties.

This work was supported by JSPS KAKENHI (JP21J01667 and JP20H02189). The HAXPES measurements were performed under approval of the NIMS Synchrotron X-ray Station (2020A4602 and 2020A4651).

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2:00pm **AA1-WeA-3 Atomic Layer Deposition of Ternary Germanium-Sulfur-Selenium and Its Application for Ovonic Threshold Switching**, ***Seungwon Park**, M. Kim, T. Kim, S. Chung, H. Kim,* School of Electrical & Electronic Engineering, Yonsei University, Korea (Republic of)

As s steep increase of memory capacity has been required, 2-terminal storage class memory (SCM) based on three-dimesional (3D) vertical cross-point (VXP) structure is receiving a lot of attention. With this regard, selector devices are an essential part of minimizing leakage current that can make failures of memory operation. Among them, ovonic threshold switching (OTS) materials consisting of chalcogenide materials (*e.g.,* S, Se, and Te) has been regarded as a promising candidate for 3D X-point owning to its low leakage and high on current (I_{on}). Nevertheless, research on atomic layer deposition (ALD)-based OTS applications, which is crucial for sophisticated thickness control and conformality, is still in the beginning stage and especially sulfur-based ALD OTS material research is lacking despite its potential to possess superior OTS characteristics.[1]

Herein, we developed a thermal ALD $Ge_{1-x}S_x$ (Ge-S) process using $HGeCl_3$ precursor and H_2S reactant. The growth characteristics and film properties of Ge-S film were investigated in detail. Besides, by incorporating thermal ALD Ge-Se designed by W.H Kim *et al.*[2] to our Ge-S, we fabricated ALD ternary germanium-sulfur-selenium (Ge-S-Se) alloy devices spanning a broad range of compositions by adjusting the ALD super-cycle ratio. The film characteristics and electrical parameters of Ge-S/Ge-Se/Ge-S-Se were evaluated and compared to verify the effect of its composition change. We successfully presented the foundation of the thermal ALD technique of Ge-S and opened the possibility to tune threshold voltage and to apply the Ge-S-Se of various composition ratios for desired purposes suitably.

Acknowledgements

This paper was a result of the research projected supported by SK Hynix Inc.

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2:15pm **AA1-WeA-4 Scaling Down to sub-5 nm Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films with Anhydrous H_2O_2 ALD Oxidant**, ***Yong Chan Jung**, J. Kim, H. Hernandez-Arriaga, D. Le, S. Hwang,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; T. Onaya,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; C. Nam, Y. Zhang,* Brookhaven National Laboratory*; S. Kim,* Kangwon National University, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

The ferroelectricity of doped HfO_2 thin films have been extensively investigated in many applications such as ferroelectric field effect transistor (FeFET), ferroelectric tunneling junction (FTJ) device, and ferroelectric random-access memory (FeRAM) etc. Previous studies have demonstrated that high-quality ferroelectric doped HfO_2 thin films can be easily obtained with a thickness of 5 nm or more.[1,2] However, it is difficult to achieve good ferroelectric property as the thickness of the ferroelectric layers decreased to sub-5 nm. In addition, the crystallization temperature increases significantly with a down-scaling of the ferroelectric film thickness due to the increase of the surface-area-to-volume ratio.[2] Therefore, we intensively investigated atomic layer deposition (ALD) process and post annealing conditions to obtain stable ferroelectric property at the $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thickness of sub-5 nm.

In this study, HZO films were deposited using anhydrous H_2O_2 as an ALD oxygen source with the variation of deposition temperature at 250 °C to 350 °C. In addition, annealing temperature was varied from 400 °C to 500 °C. To confirm robust ferroelectric property, we fabricated TiN/HZO/TiN capacitors and characterized electrically (PE hysteresis, Pulse, CV and IV analysis). The crystallinity of HZO films were also analyzed using synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) at the

Brookhaven National Laboratory. In addition, the half-cycle study using *in-situ* reflection absorption infrared spectroscopy (RAIRS) has revealed that anhydrous H_2O_2 forms high surface saturation. It is suspected that this chemical densification gives the advantages of scaling and low thermal budget of ferroelectric HZO film. The detailed results will be presented.

This work was supported by the Technology Innovation Program (20010806) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also partially supported by GRC-LMD program (#3001.001) of SRC, and the National Research Foundation of Korea (NRF) grant funded by MSIT (NRF-2019R1F1A1059972).

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2:30pm **AA1-WeA-5 Engineering the Ferroelectric Properties in Hafnium Oxide by Co-Doping during Atomic Layer Deposition**, ***Kati Kühnel***, *M. Lederer, A. Pourjafar, K. Mertens, F. Schöne, M. Neuber, L. Roy, T. Kämpfe, K. Seidel, M. Czernohorsky,* Fraunhofer IPMS, Center Nanoelectronic Technologies, Germany

The presence of ferroelectricity in hafnium oxide thin films can be controlled via doping. Since those layers are usually deposited via atomic layer deposition, the doping element (like Zr, Al, Si, La) is supplied via monolayers. This way, the metastable ferroelectric phase can be stabilized. However, often wake-up effects and asymmetries like imprints are present in the produced films, impairing optimal device performance in e.g. embedded non-volatile memory devices like ferroelectric field effect transistors. These imperfections will also affect the device behavior in piezo- and pyroelectric sensors and actuators.

We report on a novel method to control the phase and the switching behavior in hafnium oxide thin films by atomic layer deposition on 300 mm wafers. By utilizing two different doping elements with strong differences in their ionic properties, especially in their ionic radius and charge with respect to Hf, the here presented co-doping process enables to tune local stresses or electric fields. This is implemented by varying the doping concentration homogeneously in the layer and implementing concentration differences within the layer. For the hafnium oxide deposition two different precursors are explored, namely hafniumtetrachloride ($HfCl_4$) and tetrakis(ethylmethylamino)hafnium(IV) (TEMAHf). Water and ozone are used as oxidizers, respectively. For the electrical characterization, the ferroelectric films are implemented in MIM stacks with TiN as electrode material. These MIM stacks are annealedat different temperatures between 650 and 1050 °C to achieve the improved ferroelectric properties.

Depending on the used processing method, alternating or block wise dopant deposition, the phase stabilization of the ferroelectric orthorhombic $Pca2_1$ phase can be influenced, as indicated by the grazing incident X-ray diffraction results.

The polarization-voltage hysteresis shape can be modified by defining favored polarization axis orientations or influencing the domain wall movement. Moreover, effects like imprint can be counteracted. This is reflected in the displacement current by the current peak position, amplitude, shape and width. Consequently, this will affect the mechanical displacement and the pyroelectric properties as well, since they are dependent on the polarization behavior.

2:45pm **AA1-WeA-6 Magnetic and Electric Properties of Atomic Layer Deposited HfO_2-Fe_2O_3 Thin Films**, ***Kristjan Kalam***, *M. Otsus, R. Rammula,* University of Tartu, Estonia*; J. Link,* National institute of chemical physics and biophysics, Estonia*; R. Stern,* National Institute of Chemical Physics and Biophysics, Estonia*; G. Vinuesa, S. Duenas, H. Castan,* University of Valladolid, Spain*; K. Kukli, A. Tamm,* University of Tartu, Estonia

Kristjan Kalam[1], Markus Otsus[1], Raul Rammula[1], Joosep Link[2], Raivo Stern[2], Guillermo Vinuesa[3], Salvador Dueñas[3], Helena Castán[3], Kaupo Kukli[1], Aile Tamm[1]

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Atomic layer deposited thin films have had a role in memory technology for quite some time, mostly as high-k dielectrics [1]. In recent years, however, such thin films have become a subject of interest as having intrinsic memory properties themselves, such as ferromagnetism and resistive switching [2-3]. HfO_2 thin films have been found to exhibit resistive switching properties [2]. Fe_2O_3 thin films have exhibited ferromagnetic properties [3]. Therefore, it is of interest to investigate if HfO_2 coupled with Fe_2O_3 would exhibit both resistive switching and ferromagnetic hysteresis in the same material sample.

Precursors to the films were $FeCp_2$ and $HfCl_4$, whereby O_3 was the oxidizer. Film thickness, elemental composition and crystal structure were evaluated. Most films exhibited ferromagnetic and/or superparamagnetic properties. Even un-doped HfO_2 could be magnetized, provided that the cubic phase was stabilized and present in the sample. Some films exhibited an electrical nonvolatile memory effect, unipolar resistive switching, where the resistance of a film can be switched between two distinct values. For example, a layered structure HfO_2+ Fe_2O_3+ HfO_2+ Fe_2O_3 was found to have both ferromagnetic and resistive switching properties.

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3:00pm **AA1-WeA-7 Atomic Layer Deposition of Antiferroelectric Perovskite Lead Hafnate Using O_2-Gas-Only as the Oxygen Precursor**, ***Nicholas Strnad***, *W. Sarney,* Army Research Laboratory*; G. Fox,* Fox Materials Consulting, LLC*; B. Hanrahan,* Army Research Laboratory*; B. Rayner,* Kurt J. Lesker Company*; R. Rudy, J. Pulskamp,* Army Research Laboratory

ALD-grown ferroelectrics have garnered much attention over the past decade due in large part to the discovery of ferroelectric doped-hafnia which has renewed interest in scalable, non-volatile, and neuromorphic memory. Nanolaminates consisting of ferroelectric, dielectric, and antiferroelectric thin films may be engineered to exhibit neuromorphic-enabling multi-state read/write capabilities, however, there are comparably few ALD processes available for archetypal antiferroelectric thin films compared to their ferroelectric and dielectric counterparts. Here, we present an ALD process to grow perovskite, antiferroelectric lead hafnate ($PbHfO_3$, PHO) using the commonly-used amide hafnium precursor tetrakis dimethylamino hafnium (TDMAH), lead bis(3-N,N-dimethyl-2-methyl-2-propanoxide) ($Pb(DMAMP)_2$) and O_2 gas as the co-precursor for both metalorganic compounds. We show that the composition may be controlled using a super-cycle consisting of *n* PbO cycles and one HfO_2 cycle. The films were deposited in an initially amorphous state with an interspersed polycrystalline PbO phase and crystallized into the perovskite state upon either furnace or rapid thermal anneal in an oxygen atmosphere. We observed dose saturation of the O_2 gas co-precursor only for extremely large exposures in excess of $3x10^9$ L. The growth per cycle (GPC) of the PHO, averaged across the supercycle, is shown to be approximately 0.5 Å. We investigate the chemical distribution and phase of the ALD PHO films before and after annealing using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS). Quantitative electrical characterization was performed on fabricated capacitor structures using 60 nm-thick PHO on a platinized substrate, which showed double-hysteresis polarization versus voltage loops with max/min polarization values of ±50 $\mu C/cm^2$ at ±16 V.

3:15pm **AA1-WeA-8 *In-situ* Half-Cycle Study of High Purity H_2O_2-based HfO_2 Atomic Layer Deposition for Hf based Ferroelectric Devices Applications**, ***Jinhyun Kim***, *Y. Jung, S. Hwang, D. Le, H. Hernandez-Arriaga, K. Tan,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; S. Kim,* Kangwon University*; J. Kim,* University of Texas at Dallas

Recently, we have reported the ALD characteristics and film properties of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) using high purity H_2O_2 and O_3. H_2O_2-based HZO showed higher GPC, lower wet-etch rate (WER), and higher film density than O_3-based HZO.[1] In comparison to H_2O, high purity H_2O_2 delivers 50% higher GPC, improved WER, and denser film from H_2O (SFig.1). H_2O_2 has low oxygen dissociation energy and high oxidation power comparable to O_3 as well as hydroxyl groups for ligand exchange reactions like H_2O, making it an ideal candidate for the oxide ALD process. Thus, an extensive study of H_2O_2 surface reactions is necessary to further investigate the reasons behind observed improvements. The conventional H_2O_2 precursor is commonly dissolved in a high content H_2O. Therefore, identifying the effects of H_2O_2 as an oxidant of ALD process from those of H_2O is a significant challenge.[2]

In this study, we have implemented high purity anhydrous H_2O_2 to better understand ALD growth mechanism, interface formation, and film properties attributed by H_2O_2 while prohibiting the effects of H_2O.

It is expected that different oxidants (H_2O_2, H_2O, and O_3) can significantly impact the overall film growth and interfacial growth behaviors. ALD processes of HfO_2 using various oxidants are monitored to examine the surface pathways of H_2O_2, H_2O, and O_3. Comprehensive surface studies of ALD-HfO_2, deposited using TDMA-Hf and oxidants on TiN substrate, are studied using an *in-situ* reflection absorption infrared spectroscopy (RAIRS) system.[3] Half-cycle study with differential and accumulated FTIR spectra will be investigated to identify the growth mechanism of different oxidants. This will allow us to observe the TiN and oxide interface formation and ligand exchange reaction while ALD process. Moreover, the FTIR spectra of the oxide bonding region will provide a better understanding of bonding density and oxide growth. Initial *in-situ* RAIRS study indicates that the surface absorption rate of H_2O_2 is significantly faster than H_2O, providing additional reaction sites during subsequent TDMA-Hf exposure steps. Eventually, the additional Hf–O bonds may increase film density, which can potentially provide enhanced film properties. Furthermore, interface formation is expected to be also observable using *in-situ* spectra of full ALD cycles by comparing the initial and bulk cycles (SFig.2).

This work was supported by Tech. Innovation Program (20010806) funded by MOTIE and GRC-LMD program (task#3001.001) through SRC. We thank RASIRC Inc. for providing the H_2O_2 source.

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ALD Applications
Room Van Rysselberghe - Session AA2-WeA
Emerging Applications of ALD

Moderators: Giuseppe Alessio Verni, ASM, Adrie Mackus, Eindhoven University, Netherlands

4:00pm **AA2-WeA-11 Mechanical Properties of ALD Coatings***, **Aile Tamm**,* University of Tartu, Estonia*; H. Piirsoo,* University of Tartu,, Estonia*; J. Kozlova, T. Jõgiaas,* University of Tartu, Estonia **INVITED**

Demand in using films grown by atomic layer deposition (ALD) for the fabrication of microelectromechanical systems has significantly increased during the past decades [1]. ALD films can be used as supporting layers (seed layers, masks, etc) as well as device's functional layers. Depending on the application, the ALD film thicknesses used may vary from nanometer-level to several hundreds of nanometers, while composition can vary from pure metal or metal oxide to several metals together in one film. For the preparation of the devices, it is often required to obtain a film that combines several specific physical properties in one film.

Mechanical properties (elastic modulus and hardness) of ALD films with a thickness from 30 up to 150 nm were measured by nanoindentation using Hysitron TriboIndenter TI980 (Bruker). The properties (thickness, morphology, composition and crystallinity) of pure oxide films, like Cr_2O_3, Al_2O_3, Ta_2O_3, HfO_2 and ZrO_2 as well as layered nanostructures, like ZrO_2-SnO_2 [2], HfO_2-ZrO_2 [3], Al_2O_3-ZrO_2 [4] Al_2O_3-Ta_2O_5, HfO_2-Al_2O_3 will be discussed.

A few of the results of the layered nanostructures studies were follows:

1. the thickness and sequence of oxide layers of the two-and three-layered laminates influenced the hardness and elastic modulus of the laminates.
2. plasma ALD processes do not give advantages over thermal ALD.

This work overviews the results obtained by studying a quite wide range of materials where the mechanical and also magnetic or optical properties of the same ALD films were explored. Using alternating layers of different metal oxides allows fine-tuning of the film properties and even obtaining a film that overcomes the performance of the pure oxide film.

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4:30pm **AA2-WeA-13 Superconducting Tantalum Nitride Prepared by Plasma ALD With RF Biasing for Quantum Applications***, **Silke Peeters**,* Eindhoven University of Technology, Netherlands*; C. Lennon, R. Hadfield,* University of Glasgow, UK*; E. Kessels, H. Knoops,* Eindhoven University of Technology, Netherlands

This contribution reports the first critical temperatures (T_c) for tantalum nitride prepared by plasma ALD and outlines the promising electrical and structural properties of this material for application as a low-loss superconducting material in quantum devices. The motivation is to further improve quantum device performance for which a reduction of material-related decoherence sources is critical. The recent demonstration of Ta superconducting transmon qubit coherence times above 0.3 milliseconds[1] calls for further exploration of Ta-based materials for quantum applications.

This work focuses on TaN, as reported T_c values for superconductivity exceed those of Ta[2]. Moreover, nitridation of superconductors has been shown to better protect against loss due to surface oxidation[3]. To our knowledge, no superconducting transition has been reported for TaN prepared by ALD. Literature on TaN prepared by techniques such as dc magnetron sputtering and pulsed laser deposition reveals that, together with resistivity, stoichiometry and crystal structure are critical film properties in achieving superconducting TaN films.

Thin TaN layers are prepared by plasma-enhanced ALD using TBTDMT and Ar-H_2 plasma at 250 °C with RF substrate biasing. A low room temperature resistivity of 221 $\mu\Omega$ cm of a 35 nm film is measured for a 20 W RF bias, which is a hundredfold improvement compared to films prepared without biasing. XPS measurements confirm that applying a substrate bias counteracts O incorporation during deposition. In addition, XPS reveals a significant increase in C content. Strikingly, these films are of (N+C):Ta ≈ 1 stoichiometry, and it is verified that C is present in Ta-C bonds. As tantalum carbonitrides display similar superconducting properties, this may provide additional opportunities of tuning layer properties. Moreover, XRD measurements show a (111) and (200) fcc crystal structure, where the cubic structure yields the highest T_c for TaN according to literature[4]. TEM analysis reveals an increase in crystal size due to substrate biasing. Preliminary liquid He four-point probe measurements on these samples indicate a T_c above 6 K.

Through substrate biasing stoichiometric fcc $Ta(C_x)N_y$ thin films of enhanced conductivity were obtained. The control of film properties and the relation with the superconducting transition will be discussed in this contribution.

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2. Thorwarth *et al. Solid State Commun.***20**, 870 (1976)

3. Wang *et al. Jpn. J. Appl. Phys.* **42**, 1843 (2003)

4. Reichelt *et al. J. Appl. Phys.* **49**, 5284 (1978)

4:45pm **AA2-WeA-14 Membrane Design by ALD for Hydrogen Purification***, L. Badouric, M. Drobek, A. Julbe, **Mikhael Bechelany**,* European Institute of Membranes, France

Hydrogen (H_2) is one of the energy vectors essential for the success of the energy transition. In less than twenty-five years, hydrogen is expected to represent 18% of the total energy consumed on the planet thus leading to possible CO_2 emissions decrease by 6 gigatonnes compared to current levels. At the same time, hydrogen energy technologies involve major environmental, research and industrial challenges. In this presentation, we will show our efforts in designing membranes by Atomic Layer Deposition (ALD) for hydrogen purification.

In view of the increasing use of hydrogen as "green energy carrier", the various aspects of its production must be considered and optimized. Indeed, the continuous separation/purification of H_2 is a key step in the production chain. When polymer (low selectivity and temperature resistance) or palladium-based membranes (more expensive and highly sensitive to sulfur compounds) cannot be used for H_2 purification, the application of inorganic or hybrid ultra-microporous membranes is a relevant option. In this context, we will present a preparation of highly selective ultra-thin prototype membranes deposited on the surface or inner porosity of commercial porous supports by Atomic Layer Deposition (ALD). The design and synthesis conditions of these membranes are optimized according to the constraints of the targeted application, in order to maximize the thermochemical stability, the abrasion resistance as well as the membranes performance (H_2 selectivity and permeability). Several examples including the development of Metal Organic Frameworks (MOFs) [1] and Palladium - based membranes [2] as well as their composites prepared by Atomic Layer Deposition (ALD) [3] will be highlighted in this presentation.

[1] Journal of Membrane Science, 2015, 475, 39–46

[2] Journal of membrane Science, 2020, 596, 117701

[3] Chemistry of Materials 2018, 30, 7368-7390

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