ALD Fundamentals
Room Auditorium - Session AF1-MoM2
New Precursors and Processes I

Moderators: Sean Barry, Carleton University, Canada, Elisabeth Blanquet, SIMaP, CNRS, University Grenoble Alpes

10:45am **AF1-MoM2-1 Atomic Layer Deposition of Ruthenium Dioxide Thin Films Based on Redox Reactions between RuO_4 and Alcohols***, **Matthias Minjauw**, N. Poonkottil, A. Werbrouck, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Ruthenium dioxide (RuO_2), the only stable oxide of Ru metal, is a workhorse in several applications including supercapacitors, catalysis, and electrochemical devices owing to its high conductivity, good chemical stability, and a work function value higher than metallic Ru.[1] However, atomic layer deposition (ALD) literature reports on this material are scarce. Existing ALD processes based on metalorganic Ru precursors demand careful tuning of the O_2 partial pressure in order to deposit RuO_2 films, because a too low O_2 partial pressure leads to Ru metal deposition. These processes often require a relatively high deposition temperature (>180°C) and suffer from significant nucleation delays.[2]

An ALD method for the deposition of RuO_2 films without any significant nucleation delay, employing alcohols and RuO_4 as reactants is presented. Using methanol and RuO_4, a growth per cycle (GPC) of 1Å is obtained, at a deposition temperature as low as 60°C (**Figure 1**). The reaction of higher chain alcohols such as ethanol, 1-propanol and 2-propanol with RuO_4 also results in RuO_2 thin films, with a GPC that increases with the number of carbon atoms in the alcohol chain. The investigated reactant combinations display typical self-saturating ALD properties. The as-deposited films are amorphous irrespective of the alcohol used but can be transformed into crystalline rutile RuO_2 by annealing in helium or in air at around 400 °C (**Figure 2**). The deposited films are conductive as evident from a value of 230 µΩ.cm measured for a 20 nm film deposited by the methanol-based process, and the conductivity improved after the anneal.

Based on a combination of in situ mass spectrometry, in situ Fourier transform infrared spectroscopy, and in vacuo X-ray photoelectron spectroscopy results, we propose a reaction mechanism for the developed process (**Figure 3)**. During the alcohol pulse, the top RuO_2 surface is partially reduced RuO_x (x<2), and the alcohol molecules are oxidized into CO_2 and H_2O on the RuO_2 surface. This reaction also leaves some carbon monoxide (CO) residues on the surface. During the next RuO_4 pulse, the CO surface species are oxidized to CO_2 and the RuO_x surface is oxidized back to RuO_2, while additional RuO_2 is deposited onto the surface.

<u>References:</u>

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2. Austin et al., *Chemistry of Materials* **2017,** *29* (3), 1107-1115.

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

11:00am **AF1-MoM2-2 Low Temperature ALD of Ni from Novel Precursors***, **Anton Vihervaara**, T. Hatanpää, K. Mizohata, G. Popov, M. Chundak, M. Ritala,* University of Helsinki, Finland

High quality metal thin films are an essential material class in the development of new technologies. Ni thin films may be used in a variety of applications, including protective coatings, catalysis and microelectronics. For example, nickel is a valid candidate for replacing copper as an interconnect material. Nickel also has ferromagnetic properties, and nickel films could be the key in the development of magnetic memories.

Out of all thin film deposition methods, ALD is the best suited for the manufacturing of complex 3D structures that are essential in future technologies. Several ALD processes for Ni metal already exist, but new ones are constantly sought out to overcome limitations of the existing ones. In order to have very thin but also completely continuous films, it is important to keep the deposition temperature low. Typically, a lower deposition temperature leads to smaller grains and thus to smoother films. Our approach focuses on novel ALD precursors, both the metal precursors and reducing agents, as the key factors limiting the deposition temperature are the reactivity and vapor pressure of the precursors.

1,4-bis(trimethylsilyl)-1,4-dihydropyrazine ($(Me_3Si)_2DHP$) is a promising reducing agent that has been used to deposit Ti and Sn films from their respective chlorides.[1,2] Reducing Ti^{4+} to metallic state is especially challenging due to its low redox potential. These studies indicated general reactivity of $(Me_3Si)_2DHP$ towards metal halides. However, in our experiments, $(Me_3Si)_2DHP$ did not work well with our nickel halide precursor at low temperatures. Instead, its germanium analogue 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine ($(Me_3Ge)_2DHP$) showed great potential as a novel powerful reducing agent.

In this study, we developed a new ALD process for Ni metal from the novel precursors $NiCl_2(PEt_3)_2$ and $(Me_3Ge)_2DHP$. Smooth nickel films were deposited on different substrate materials at 110 °C which is the lowest deposition temperature for Ni metal found in the literature. ALD characteristics were confirmed and saturation achieved with both precursors. Growth rate is 0.2 Å/cycle when the film is not continuous and decreases to 0.1 Å/cycle after the film becomes pinhole-free. Besides a small amount (7 at.%) of carbidic carbon, the films have only small amounts of impurities. Most notably the chlorine content is below 0.2 at.%. Furthermore, $(Me_3Ge)_2DHP$ shows promising results with other metal halide precursors too, and can therefore open new avenues for ALD of metals at low temperatures.

[1] E. C. Stevens et al., *J. Vac. Sci. Technol. a*, 2018, **36**, 06A106.

[2] J. P. Klesko et al., *Chem. Mater.*, 2015, **27**, 4918–4921.

11:15am **AF1-MoM2-3 Enhanced Cation Control in ALD of Alkali Metal Containing Films by Avoiding Water-Reservoir Effects***, **Henrik H. Sønsteby**,* University of Oslo, Norway

Alkali metal containing the films get increasing attention in a world moving towards green- and sustainable energy and chemistry. Lithium containing thin films are important as e.g. solid electrolyte interface layers in batteries. Sodium containing materials may provide low-cost options for the next generation of batteries, and some potassium compounds are important ferroelectrics that may abolish the lead-hegemony within sensors and actuators. The heavier alkali metals, rubidium and cesium, are crucial components in perovskite solar cells and may also provide routes to novel functional perovskite materials.

As important as they may sound, alkali metal containing compounds (with the exemption of lithium) has seen very little activity within the ALD community. ALD processes for Na and K were introduced in 2014, and was followed by Rb and Cs in 2018 and 2020, respectively. Processes for important functional materials like NaCoO2, (K,Na)NbO3 and K(Ta,Nb)O3 have been developed, but all of them struggle with loss of control due to significant water reservoir effects. This is due to strong hygroscopicity of intermediary species, storing water in the films that react with the alkali metal precursors during deposition. In some cases this may be controlled by careful process optimization, but this severely compromises the reproducibility of published processes.

In an attempt to remove the water reservoir effects, we have developed new processes for alkali metal containing thin films. These make use of the same alkali metal precursors as before (t-butoxides), but removes water outright, relying on O3 as the oxygen source. We observe that this completely eliminates the water reservoir effect, giving a much more stringent process control. This means that there are no changes in the process chemistry during deposition, leading to homogeneous films with easier access to controlled tuning of the cation composition.

In this talk, I will use in situ metrology and ex situ diffraction studies to show how these new ozone based processes provide far superior alkali metal containing thin films. I will use the complex oxide K(Ta,Nb)O3 as an example, providing significant impact as an important component in electrooptical applicaitons. I will show that crystallinity and epitaxy is achieveable at lower temperatures than with the water based process, with much higher compositional control.

These findings are important in a wide range of fields, from sustainable energy to next generation electronic devices, where ALD will play a crucial role in the development of new devices.

11:30am **AF1-MoM2-4 Atomic Layer Deposition of Lead Halides: $PbBr_2$ and $PbCl_2$***, **Georgi Popov**, C. Van Dijck, L. Junkers,* University of Helsinki, Finland*; G. Bačić,* Carleton University, Canada*; A. Weiss, M. Mattinen, A. Vihervaara, P. Jalkanen, K. Mizohata, J. Räisänen, M. Kemell, M. Leskelä,* University of Helsinki, Finland*; S. Barry,* Carleton University, Canada*; M. Ritala,* University of Helsinki, Finland

In our previous work we used lead(II) bis[bis(trimethylsilyl)amide], $Pb(btsa)_2$, and tin(IV) iodide for ALD of PbI_2.[1] We hypothesized that similar chemistry is straightforwardly extendable to ALD of other metal halides. Here we put this hypothesis to the test by using analogous chemistry for ALD of $PbBr_2$ and $PbCl_2$. The chemistry can indeed be extended to these lead halides, but we also encountered a number of technical challenges and unexpected outcomes.

The vapor pressure of $SnBr_4$ made ALD of $PbBr_2$ from $SnBr_4$ and $Pb(btsa)_2$ challenging in our ALD reactors. The vapor pressure of $SnBr_4$ is too high for internal hot source and too low for external cold source. Therefore, for ALD of $PbBr_2$ we employed $TiBr_4$, a compound very similar to $SnBr_4$ but with a lower vapor pressure. $TiBr_4$ could be delivered from a hot source. The $PbBr_2$ films deposited with $Pb(btsa)_2$ and $TiBr_4$ are uniform, pure and crystalline. The $PbBr_2$ process displays characteristics typical for an ALD process such as saturation of the growth per cycle values with respect to precursor doses.

Development of an ALD process for $PbCl_2$ required the largest research effort. $Pb(btsa)_2$ and $SnCl_4$ did deposit $PbCl_2$, but the process did not show saturative behavior and had other non-ideal features. With a new lead precursor bis[lead(II) *N,N'*-di-*tert*-butyl-1,1-dimethylsilanediamide], $(Pb(gem))_2$[2], the deposition was saturative but the films contained tin. Similarly, a process using $Pb(btsa)_2$ and $TiCl_4$ suffered from titanium incorporation.

As a last-ditch effort we tried $GaCl_3$ as the chlorine source. The quality of the first films grown with $GaCl_3$ was disastrous, however relatively minor gallium incorporation encouraged us to continue our pursuit for a $PbCl_2$ ALD process. Through a series of optimizations in the $GaCl_3$ delivery system we were able to develop a process that produces crystalline, pure and uniform $PbCl_2$ films and has the characteristics typical for ALD. Additionally, the optimized delivery system solved the challenges associated with the use of $SnBr_4$.

Our interest in ALD of lead halides is application driven. Various post treatments can convert lead halides into halide perovskites, materials with outstanding opto-electronic properties, that can be improved even further in mixed halide perovskites.[3] We are currently studying whether combining ALD processes of different lead halides and post processing of the resulting films will afford perovskites with mixed composition such as $CH_3NH_3PbI_{3-x}Br_x$.

[1] Popov et al. Chem. Mater. **2019.** 10.1021/acs.chemmater.8b04969

[2] Bačić, PhD Thesis, Carleton University **2021**. 10.22215/etd/2021-14420

[3] Zarick et al. *J. Mater. Chem. A.* **2018**. 10.1039/c7ta09122b

11:45am **AF1-MoM2-5 Carbene Based Precursors for the ALD of Coinage Metals*, Nils Boysen,*** Ruhr University Bochum, Germany*; A. Philip,* Aalto University, Finland*; D. Rogalla,* Ruhr University Bochum, Germany*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Thin layers of coinage metals like copper and silver are of immense importance for a variety of technological applications. While the atomic layer deposition (ALD) of copper thin films is fairly well developed and several suitable copper precursors are known, the same is not true for silver. The very limited number of silver precursors which combine a high thermal stability, volatility, and reactivity has been a hindrance for the convenient fabrication of silver thin films by ALD. Seen from a chemical perspective, organometallic Cu(I) and Ag(I) compounds feature remarkable similarities in their structure, ligand-to-metal interaction, and reactivity.

In this study, we opted for a systematic transfer of structural motifs from N-Heterocyclic carbene (NHC) stabilized copper(I) complexes bearing anionic diketonate ligands to the resulting isostructural Ag(I) complexes, while the structure, thermal properties and reactivity was comparatively analyzed. As a result, five new monomeric Cu complexes and four new isostructural Ag complexes with the general formula [M(NHC)(diketonate)] (M = Cu, Ag) were successfully synthesized (Scheme 1). Through a rational and incremental change of the substitution pattern of the anionic backbone based on diketonates, clear trends in their structural and thermal parameters could be observed. Nuclear magnetic resonance (NMR) spectroscopy, single-crystal X-ray diffraction (SC-XRD) and electron-impact mass spectrometry (EI-MS) revealed a first interesting trend in the bonding and structure of the complexes: Despite featuring a monomeric nature in the solid, liquid, and gaseous phase, differences in structure, bond lengths and bond angles were observed depending on the employed metal for complexation. An extensive search in the Cambridge Structural Database (CSD) enabled to ascertain the differences seen in bonding between the isostructural Cu and Ag complexes while revealing additional similarities and differences. The evaporation profile and thermal characteristics as analyzed by thermogravimetric (TG) measurements highlight that the Cu complexes feature a higher thermal stability compared to the isostructural Ag analogs (Figure 1). Proof-of-principle ALD with [Cu(NHC)(acac)] was carried out at low temperatures (145 °C) for depositing metallic Cu using hydroquinone as the reducing agent which were subsequently analyzed by XRD, SEM (Figure 2) and RBS/NRA.

The findings from this study set a new milestone in the understanding of the influence of systematic anionic ligand choice on the applicability of Cu(I) and Ag(I) precursors in vapor-phase deposition processes.

12:00pm **AF1-MoM2-6 Low Temperature ALD of Metals and Nitrides Using Thermally Generated Radical Precursors*, Goran Bacic,*** Carleton University, Canada*; C. Dezelah,* ASM Microchemistry Ltd., Finland*; S. Barry,* Carleton University, Canada

Radicals are the main reactive species in remote plasma-enhanced atomic layer deposition (PEALD). The highly reactive nature of radicals can enable deposition at substantially reduced temperatures compared to thermal ALD. However, plasma-generated radicals are unstable transient species that can have limited diffusion, causing non-uniform deposition inside small features like trenches and vias. To overcome the limitations of plasma-generated radicals, we propose to harness the reactivity of these species more effectively by designing precursors that thermally generate radicals directly inside the deposition chamber.

In this presentation, we will report our efforts to design thermal H• and •NH_2 radical-generating precursors for ALD of metals and nitrides, respectively. A good thermal radical precursor should generate a stable radical species that itself does not react further with the growing film or substrate, analogous to spectator ions in solution. While stable radical chemistry in solution has a rich and diverse history, there is little precedent for the use of radicals or their precursors in the synthesis of metal and nitride materials, and there was virtually no description of their use in the gas phase. Moreover, the factors that reportedly influence radical stability (e.g., extended π-systems, huge steric bulk) are at odds with traditional precursor design.

We took a concerted theoretical and experimental design approach and propose several precursor candidates displaying many or all of the desired properties: small E—H or E—NH_2 homolytic bond dissociation enthalpies (BDE < 70 kcal/mol), high volatility ($T_{1Torr} < 100$ °C), high thermal stability ($T_{dec} > 300$ °C), high reactivity ($T_{ALD} < 300$ °C), low cost (<4 steps to synthesize), and low health and environmental risk. Volatility and thermal stability were determined by thermogravimetric analysis (TGA), with most precursors achieving a vapor pressure of 1 Torr below 100 °C and showing thermal stability up to at least 300 °C. We explored solution-phase reactivity toward industrially relevant ALD precursors by NMR spectroscopy and further studied precipitates from these solution test reactions by SEM and TEM. ALD process development using a commercial reactor for each precursor was accelerated by in-situ quartz crystal microbalance (QCM) analysis. Finally, due to their highly reactive nature, special attention was given to synthesis scale-up and potential health and environmental risks of our best precursors.

ALD Fundamentals

Room Van Eyck - Session AF2-MoM2

High Aspect Ratio/High Surface Area/Powder ALD

Moderators: Jolien Dendooven, Ghent University, Belgium, Juhani Taskinen, Picosun Oy

10:45am **AF2-MoM2-1 Influence of the High Aspect Ratio Geometry to ALD Thin Film Growth*, Oili Ylivaara,*** VTT Technical Research Centre of Finland*; M. Utriainen, P. Hyttinen,* Chipmetrics Oy, Finland*; R. Puurunen,* Aalto University Aalto School of Chemical Engineering, Finland

ALD is a thin film growth method enabling device down-scaling beyond Moore's law[1]. Device down-scaling gives boundary conditions to thin film quality in a sense of film uniformity, conformality and homogeneity, which need to be characterized even a few nanometers thin. Shrinking device dimensions and film thicknesses set new challenges to process development and quality control as thin film analysis and characterization becomes challenging. PillarHall™ LHAR test structure has proven its value in ALD conformality characterization[2-4]. High aspect ratio (HAR) geometry in PillarHall has characteristically infinitely wide trench with height of 500 nm and width of 10 mm. However, in real applications the geometry and pitch size vary. The question is how variable HAR geometries correlate with PillarHall in conformality and ALD growth analyses? In this study, we used nanolaminate ALD process and set of variable high aspect ratio test structure geometries as substrates. Thermal ALD Al_2O_3-TiO_2 nanolaminate growth was studied at three different temperatures, at 110, 200 and 300 °C. Targeted film thickness was 25 nm. For nanolaminate, sublayer thicknesses were targeted to 1 nm both for Al_2O_3 and TiO_2. For comparison results were compared with LHAR chips coated with reference ALD Al_2O_3 grown at 300 °C. Five different conformality test chip designs were coated in a one run and analyzed: PillarHall LHAR4 with three different channel heights namely 100, 500 and 2000 nm. A prototype PillarHall LHAR3 test chip with narrow lateral channels widths from 2 to 78 µm (so called FIN-design) and vertical HAR (VHAR) test structure of an array of vertical pores, 1 µm in diameter and 219 µm in depth. During the coating chips were place in center of the wafer holder to minimize the conformality variation at the wafer surface level. After the coating LHAR samples were analyzed by optical microscopy, spectroscopic reflectometry, and for VHAR samples electron microscopy cross-section was used. We show that with PillarHall, we can study in more detail the film growth in the channel, geometry dependence and study the process saturation in the channel. We also study of applicability of narrow channels of FIN-design, width from 2 to 78 µm, and compare the results with the Gordon model[5].

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11:00am **AF2-MoM2-2 Ultra-Low Temperature ALD of Pure Antimony for Grain Boundary Engineering of Thermoelectric Materials***, **Amin Bahrami**, S. He, R. He, S. Lehmann, K. Nielsch,* Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e. V., Germany

Antimony (Sb) in thin film form is considered as a nano-optical material which is of interest for potential applications, such as photonic computing or high-speed holographic displays. It has been used as lens material in super-resolution near-field structures and broadband saturable absorber among others. In addition to optoelectronic properties, Sb is widely used as a dopant in tuning the transport properties of many thermoelectric materials such as PbTe, Half-Heusler compounds and so on. In this study we propose new ALD formulation for low temperature deposition of pure Sb down to 70 °C making this process applicable on the surface modification of low and medium temperature thermoelectric materials such as Mg_2Sb_3, Bi_2Te_3. Pure and conformal thin films of elemental Sb were prepared by ALD using $Sb(OEt)_3$ and $(Et_3Si)_3Sb$ as precursors with a growth per cycle (GPC) of 0.18 Å at deposition temperature of 70 °C. The electrical conductivity of the films grown on mica at 70 °C ($1.13´10^4$ S/cm) is slightly higher than that of reported by Pore *et al.* ($1.07´10^4$ S/cm). NbFeSb half-Heusler particles were successfully coated with ultra-thin layer of Sb and consolidated using high pressure sintering techniques. The results show addition of few atomic layer of Sb on NbFeSb particles can significantly enhance the electrical conductivity of the studied half-Heusler compound which was reduced during the high-pressure sintering.

11:15am **AF2-MoM2-3 Infilling Macroscopic Nanoparticle Networks via ALD***, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Nanocomposites formed by infilling nanoparticle networks have unique thermal, mechanical, optical, and electronic properties. Typically, the networks are substrate-supported nanoparticle thin films with thickness on the order of 1 µm or less, and infilling is accomplished via ALD precursor dose times on the order of 1 s. In this work, we investigate the infilling of nanoparticle networks that are at least 1,000 times thicker. We press metal oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with >1 mm thickness and ~50% solid volume fraction, and we coat the pores with ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for several minutes per half-cycle. For comparison, we also produce an alternative nanocomposite by first coating the metal oxide nanopowder with ZnO in a particle ALD rotary reactor and then pressing the resultant core/shell nanopowder into a porous compact. In both cases, we use scanning electron microscopy, energy-dispersive X-ray spectroscopy, and electrical conductivity measurements to evaluate the uniformity and connectivity of the ZnO networks that form within the nanocomposites. Additionally, we examine ALD precursor diffusion and reaction kinetics and estimate saturation times through analysis of the deposition chamber pressure traces, and we compare our empirical findings to predictions based on a Knudsen diffusion model.

11:30am **AF2-MoM2-4 Zinc Acetylacetonate on Mesoporous Supports by Atomic Layer Deposition***, **Jihong Yim**, E. Haimi,* Aalto University, Finland*; M. Mäntymäki,* University of Helsinki, Finland*; V. Kärkäs,* Aalto University, Finland*; R. Bes,* University of Helsinki, Finland*; A. Arandia, J. Velasco, T. Viinikainen,* Aalto University, Finland*; S. Huotari,* University of Helsinki, Finland*; R. Karinen,* Aalto University, Finland*; M. Putkonen,* University of Helsinki, Finland*; R. Puurunen,* Aalto University, Finland

The self-terminating nature of atomic layer deposition (ALD) enables the preparation of uniform coatings on high-surface-area materials.[1] Our general aim is to use ALD to prepare zinc promoted heterogeneous catalysts for carbon dioxide hydrogenation into methanol.[2] In this work, we aimed to obtain uniform coating of zinc on mesoporous monoclinic zirconia and gamma alumina particles in a fixed-bed flow-type ALD reactor.

Zinc acetylacetonate [$Zn(acac)_2$], a non-toxic reactant with a good stability in air, was used as an ALD reactant. Thermogravimetric analysis confirmed $Zn(acac)_2$ to be a potential reactant. $Zn(acac)_2$ was vaporized at 120 °C and carried by N_2 to the calcined support for 3 h. For zirconia, the effect of the calcination temperature (400 to 1000 °C, typically 600 °C), process temperature (160 to 240 °C, typically 200 °C), and number of cycles (1-3, 2nd reactant: oxygen) on zinc loading were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). For zirconia and alumina, the amount of $Zn(acac)_2$ evaporated was varied. Zinc distribution within a solid support particle was analyzed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Fig. 1 and Fig. 2 of the supplementary information). A diffusion-reaction model[3,4] was used to simulate the saturation profile of zinc within theoretical pores (Fig. 3). Electronic structure of zinc was analyzed by X-ray absorption spectroscopy (XAS). The oxidation of acac ligands on the samples was observed by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with mass spectrometry (MS). The zinc content on zirconia saturated to ca. 1.3 wt-% (2.2 Zn nm^{-2}) with increasing amount of $Zn(acac)_2$. The zinc content decreased from ca. 2.2 to 0.3 wt-% with increasing calcination temperature, most likely resulting from the decreasing zirconia surface area. The zinc areal number density (ca. 2.2 Zn nm^{-2}) remained almost constant.

This work was supported by the Academy of Finland (COOLCAT project, grant no. 329978, ALDI project, grant no. 331082, and Matter and Materials, grant No. 318913) and by R. L. Puurunen's starting grant at Aalto university. Hannu Revitzer and Ilkka Välimaa are thanked for the ICP-OES analysis.

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4. J. Yim and E. Verkama et al., submitted. Preprint DOI: 10.33774/chemrxiv-2021-2j4n1.

11:45am **AF2-MoM2-5 Synthesis of High Surface Area Metal Oxide Catalyst Supports***, **Robert Baumgarten**, P. Ingale, K. Knemeyer, R. Naumann d'Alnoncourt, M. Driess,* BasCat – UniCat BASF JointLab, Technische Universität Berlin, Germany*; F. Rosowski ,* BASF SE, Process Research and Chemical Engineering, Germany

Group 13 metal oxides (e.g. Al_2O_3, Ga_2O_3 and In_2O_3) are utilized for a broad range of electronic applications such as semiconductors, optoelectronics and sensors. Besides, they represent essential components of heterogenous catalysts. Al_2O_3 is employed industrially as support material or catalyst itself for various reactions like epoxidation of alkenes and dehydration of alcohols [1]. Moreover, Ga_2O_3 has been intensively studied for the dehydrogenation of light alkanes and In_2O_3 catalysts gained a lot of attention due to the ability of converting CO_2 into methanol [2, 3].

In heterogeneous catalysis, reactions mostly occur at active sites on the material's surface. Therefore, high surface area and homogeneous dispersion of deposited interfaces (e.g. metal oxides) are decisive for enhanced activity [4]. Yet, standard synthesis techniques like impregnation and precipitation often lead to unwanted agglomeration. One well-established technique which overcomes uncontrolled coating is atomic layer deposition (ALD). ALD leads to uniform, nanoscale films on a materials surface and is therefore progressively attracting attention as potential synthesis-tool for catalysts [5]. However, most ALD investigations target flat substrates whereas for catalyst synthesis, powders with high surface area and porosity are demanded.

In order to enable the full potential of ALD-synthesized catalysts, the deposition behavior on porous powders has to be further elucidated. Previously, we demonstrated the growth behavior of AlO_x on mesoporous silica using the ALD process of trimethylaluminum and water [6]. In the current study, we approach other catalytically active oxides of group 13 metals like gallium (GaO_x) and indium (InO_x). Both oxides were deposited on high surface area silica powder *via* ALD and their growth behavior was studied intensively using *in-situ* thermogravimetry, XRD, STEM, FTIR and NMR. Furthermore, both processes were compared to the powder ALD process of AlO_x and reference samples prepared *via* incipient wetness impregnation.

References

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12:00pm **AF2-MoM2-6 ALD on Porous Substrates: From General Formulation to Fibrous Substrates and Scaling Laws***, **Wojciech Szmyt**, C. Guerra-Nuñez,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; L. Huber,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Dransfeld,* TU Delft, Netherlands*; I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

In order to achieve the uniform coating in the ALD process, a sufficient gas exposure (exposure time and gas concentration) needs to be provided. This requirement becomes particularly relevant for highly porous and high aspect-ratio substrates, where the gas transport into the substrate structure is limited by diffusion (diffusion-limited regime), or for ALD precursor systems exhibiting low surface reaction rate (reaction-limited regime). This work (Szmyt *et al*., Chem. Mat. 2022, 34, 1, 203-216) reports how the distinction between diffusion- and reaction-limited ALD regimes is directly quantitatively related to the width of the reaction front and the profile of chemisorption coverage in a single cycle ALD, all of them being determined by the natural length unit of the system. We introduce a new parametrization of the system based on its natural system of units, dictated by the scales of the physical phenomena governing the process. We present a range of scaling laws valid for a general porous substrate, which scale intuitively with the natural units of the system. The scaling laws describe (i) the coating depth in a diffusion-limited regime with respect to the gas exposure, (ii) the chemisorption coverage in a reaction-limited regime with respect to the gas exposure, and (iii) the width of the reaction front in the diffusion-limited regime. For the first time, the distinction between diffusion- and reaction-limited ALD regimes is directly quantitatively related to the width of the reaction front and the profile of chemisorption coverage in a single cycle ALD. The model system for the multicycle diffusion-limited coating of random fibrous mats was validated with an experiment of ALD on a forest of tortuous carbon nanotubes (CNTs).

ALD Fundamentals
Room Auditorium - Session AF1-MoA
New Precursors and Processes II

Moderators: Romain Gaillac, Air Liquide, Mikko Ritala, University of Helsinki

1:30pm **AF1-MoA-1 Atomic Layer Deposition of CsI and $CsPbI_3$,** ***Alexander Weiß****, G. Popov, E. Atosuo, P. Jalkanen, A. Vihervaara, M. Vehkamäki,* University of Helsinki, Finland*; H. Sipilä, A. Niemela,* Fenno-Aurum Oy Ltd, Finland*; M. Ritala, M. Kemell,* University of Helsinki, Finland

Cesium iodide (CsI) is one of the most studied and applied scintillator materials. It exhibits a band gap located in the UV region (5.42 eV) and an outstanding detective quantum efficiency (DQE). Owing to these properties CsI was established as material of choice for indirect x-ray imaging in radiology[1], amongst other applications. Moreover, CsI thin films are precursors to some halide perovskite absorbers that are used in Perovskite Solar Cells (PSCs). This young research field recently gained high interest because of the potential to deliver low-cost solar energy. However, there are still two challenges for PSCs to become widely commercially available: The difficulty in scaling-up and the instability of the perovskite in ambient conditions.

Our approach to tackle the scalability issue relies on Atomic Layer Deposition (ALD) because of its high controllability to deposit thin films on large areas and complex-shaped surfaces. We believe that developing an ALD process for CsI can also address the stability issue: Literature reports give evidence that perovskite solid solutions have better stability than pure perovskites. Key to these solid solutions is the controlled addition of several cations and/or anions into the perovskite structure. In our previous work, we already demonstrated an ALD process for PbI_2 thin films and its conversion into methyl ammonium lead iodide $CH_3NH_3PbI_3$ (MAPI)[2]. Developing an ALD process for CsI and combining it with the PbI_2 process to deposit $CsPbI_3$ would be the first step towards depositing solid solution perovskites with ALD from $CsPbI_3$ with MAPI.

In this work, we report a new ALD CsI process that uses cesium bis(trimethylsilyl) amide (Cs(btsa)) as the cesium precursor and tin(IV) iodide (SnI_4) as the iodine precursor. The high volatility of Cs(btsa) enables deposition of phase pure CsI at low temperatures (140 °C). In the range of 150 – 170 °C the process exhibits a temperature independent growth per cycle (GPC) value of 3.3 Å. The GPC saturates rapidly with respect to both precursor pulses and purge durations, and is independent of the number of deposition cycles. Furthermore, we demonstrate the deposition of ternary $CsPbI_3$ perovskite thin films with a two-step approach: First, we deposit CsI thin film via ALD. In the second step, the CsI film is exposed to our previous PbI_2 ALD process yielding directly $CsPbI_3$ perovskite. This combination of CsI and PbI_2 ALD allows to prepare phase pure γ-$CsPbI_3$ and δ-$CsPbI_3$ thin films, depending on the number of PbI_2 deposition cycles.

[1] Keiko et al. *U. S. Patent Appl. Publ.* **2011**. US20130068953A1

[2] Popov et al. *Chem. Mater.* **2019**, *31* (3), 1101-1109.

1:45pm **AF1-MoA-2 Co(II) Amide, Pyrrolate, and Aminopyridinate Complexes: Assessment of Structure and Thermal Properties as ALD Precursors*, ****Jorit Obenlüneschloß****, D. Zanders,* Ruhr University Bochum, Germany*; M. Land, S. Barry,* Carleton University, Canada*; A. Devi,* Ruhr University Bochum, Germany

Thin films of cobalt metal are subject of high research and economic interest owing to their potential to facilitate performance increases in integrated circuitry (IC) devices at continuously shrinking dimensions. Its good conductivity and stability are among the reasons cobalt is handled as a replacement to copper. To implement cobalt thin films, atomic layer deposition (ALD) is a favorable fabrication technique allowing precise device architectures to be coated uniformly with sub nanometer thickness control.[1]

In ALD, the choice of precursor is of crucial importance because its thermal behavior and reactivity are paramount for successful deposition of a desired thin film material. Revisiting the library of Co precursors, all nitrogen coordinated precursor complexes are underexplored; surprisingly as Co(II) diazadienyls have successfully ventured into the field.[2]

Motivated by this premise, we studied a variety of new nitrogen coordinated Co complexes and their potential for ALD. They have been synthesized and thoroughly characterized by EA, EI-MS, SC-XRD, TGA and vapor pressure estimations.[3]

An entry point to this study was found in the Co(II) bis(trimethysilyl)amide dimer **1**. This very compound was reacted with a selection of amides, imides, amide-adducts, pyrroles, and amido-amines (Fig. 1). With structural and chemical ligand variations in the form of aromatic moieties, varying ring size, substitution patterns, bonding character and strategic incorporation of silylamide functionalities, a variety of cobalt compounds was successfully obtained (Fig. 1). The modifications were performed to gain a broader understanding of influences on reactivity, stability, and volatility with the aim of tailoring the compounds suitable for ALD.

Whereas some of the forwarded complexes followed the expected structural trends, others adopted distinctive and unexpected coordination motives (Fig. 2). This was reflected by their thermal behavior and underlined that gradual ligand alteration can have a vast impact Additionally, the assessment of volatility also shows distinct differences between the employed ligands (Fig. 3). Especially volatile with high stability were the Co(II) iminopyrrolate **9** and the silylamido-amine **11**. Those two newly uncovered precursors were found to be especially promising candidates for application in ALD process development.

[1] A. E. Kaloyeros, et al., *ECS J. Solid State Sci. Technol.***2019**, *8*, 119–152.

[2] J. P. Klesko, et al., *Chem. Mater.***2016**, *28*, 700–703.

[3] D. Zanders, J. Obenlüneschloß, et al., *Eur. J. Inorg. Chem.***2021**, 5119–5136.

2:00pm **AF1-MoA-3 SnO Thin Films *via* Water Based ALD using a Sn(II) Precursor: Precursor Evaluation and ALD Process Development*, ****Niklas Huster****,* Ruhr University Bochum, Germany*; R. Ghiyasi,* Aalto University, Finland*; D. Zanders,* Ruhr University Bochum, Germany*; D. Rogalla,* RUBION, Ruhr University Bochum, Germany*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Tin(II) oxide is one of the few p-type semiconducting materials that possesses excellent electrical and optical properties. Hence this interesting material system is very appealing for applications in chemical sensing, as anode material for Li-ion batteries or as a transparent conductive oxide (TCO) in thin film transistor (TFT's), particularly due to the high hole mobility. Nevertheless, the deposition of stoichiometric SnO thin films is a challenging task. Atomic layer deposition (ALD) is a preferred process for thin film deposition as it is capable of yielding high quality, dense and uniform layers with an excellent control over film thickness as well as the ability to control the stoichiometry. Sn(II) oxide readily oxidizes to Sn(IV) and there are not many ALD processes known for obtaining highly stoichiometric SnO films. Thus, care must be taken with respect to process parameter selection and precursor choice.

Herein, we report the successful deposition of stoichiometric SnO thin films in a simple water based ALD process, employing the homoleptic, liquid tin(II) formamidinate precursor $[Sn(^iPr_2fAMD)_2]$ that was recently reported for ALD of SnS.[1]. Based on the promising thermal properties (Figure 1), good thermal stability and high reactivity towards water, we employed this precursor for ALD of SnO. The newly developed ALD process yielded SnO layers in the temperature range of 120 °C to 180 °C on Si substrates. The formation of tetragonal romachite-type SnO films was confirmed by Grazing Incidence X-ray Diffraction (GI-XRD) while surface and bulk composition were verified by means of X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS) / Nuclear Reaction Analysis (NRA) (Figure 2). The films were found to exhibit the desired stoichiometry alongside high purity. Optical bandgaps of as-deposited and annealed films were determined *via* Tauc-plotting from UV-Vis measurements. This is a very promising ALD process development where the role of precursor and co-reactant choice enabled the phase control of SnO films.

[1]Kim *et al.*, *ACS Appl. Mater. Interfaces*, **2019**, 11, 45892–45902

2:15pm **AF1-MoA-4 Tuning the Texture of ZnO Thin Films Through the Addition of a Volatile Shape-Directing Agent in the AP-SALD System***, C. Crivello, M. Weber,* LMGP Grenoble-INP / CNRS, France*; T. Jalabert, G. Ardila Rodriguez,* IMEP-LaHC UGA/CNRS/Grenoble INP, France*; M. Dibenedetto, ****David Muñoz-Rojas****,* LMGP Grenoble-INP / CNRS, France

Zinc oxide draws attention for its relatively low cost, the wide bandgap of 3.37 eV,[1] and for its electrical and optical properties for applications such as gas sensors, solar cells, thin-film transistors and light-emitting diodes.[2,3] ZnO thin films can be obtained by different deposition methods, from sol-gel approach to sputtering, and gas-phases based approaches such as molecular beam epitaxy (MBE), chemical vapour deposition (CVD), atomic layer deposition (ALD).

Within the materials deposition techniques, Atmospheric Pressure Spatial ALD (AP-SALD) is gaining momentum since it is a high throughput and low-cost alternative to conventional ALD. AP-SALD is based on a physical separation (rather than temporal separation, as is the case in conventional ALD) of gas-diluted reactants over the surface of the substrate by a region containing an inert gas.[4]

In this presentation, we will show that a volatile shape-directing agent can be used to tune the texture and growth rate of ZnO thin films deposited by AP-SALD. While the use of such agents is common in liquid-based synthesis approaches, their use in the AP-SALD system has never been used to the best of our knowledge. (002)-oriented hexagonal wurtzite-type ZnO films were obtained at 200 °C, without any post-deposition treatment.

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[2]Zhao M-J, Sun Z-T, Hsu C-H, Huang P-H, Zhang X-Y, Wu W-Y, et al. Zinc Oxide Films with High Transparency and Crystallinity Prepared by a Low Temperature Spatial Atomic Layer Deposition Process. Nanomaterials 2020;10:459. doi:10.3390/nano10030459.

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2:30pm **AF1-MoA-5 Recent Advances in Rare Earth Precursors for ALD***, **Jean-Pierre Glauber**, M. Schmickler, P. Kaur, S. Beer, N. Boysen,* Ruhr University Bochum, Germany*; A. Devi,* Ruhr Universität Bochum, Germany

Rare earth (RE) containing thin films are indispensable for several different applications owning to their broad number of intrinsic functional properties. Especially, RE-oxides and -sulfides are of high interest for various applications such as high-κ dielectrics (Y_2O_3, CeO_2), optical fibers in lasers (Yb_2O_3), spintronics (EuS) or photovoltaics (Nd_2S_3). However, to gain fundamental insights and accelerate the development of these devices, reliable synthesis routes that yield high-quality material are required.[1] Vapor phase deposition methods such as atomic layer deposition (ALD) can meet these demands, but to develop promising processes for the formation of the RE-containing materials, precursors with certain pre-requisites are of utmost importance.[2] Besides sufficient volatility and thermal stability at the operating conditions, the precursors need to exhibit a high reactivity towards the employed co-reactant.

Commonly used ligands with oxygen-metal bonds suffer from a low reactivity towards the co–reactants due to strong RE–O bonds, which limits their applicability in ALD processes. On the other hand, precursors with guanidinate (dmg), amidinate (amd) and formamidinate (famd) ligand moieties have gained prominence since their all-nitrogen coordinated ligands ensure high reactivity toward mildly reactive co-reactants such as H_2O, while retaining volatility and thermal stability.[2,5]

Consequently, a series of RE containing precursors, with the formula $[M(L)_3]$ (M = Y, Ce, Eu, Yb; L = dpdmg, dpamd, dpfamd) were synthesized (Figure 1), structurally analyzed, and their thermal properties evaluated.[1-5] Furthermore, the tunability of the thermal properties via a variation of the ligand side chains was demonstrated for Y formamidinates [3] as well as for amidinates and guanidinates of Ce and Yb [2] with systematic thermogravimetric analysis studies (TGA).

Density functional theory (DFT) calculations of the reaction between selected Y, Yb and Ce precursors with H_2O revealed a pronounced reactivity towards mild oxidizing agents and underlined their suitability for ALD processes.[2,3] Actual ALD experiments of Y formamidinate- and Ce guanidinate-based precursors with H_2O as the co-reactant confirmed the results from DFT and yielded high-quality thin films of Y_2O_3 [3,4] (Figure 2) and CeO_2 [2], respectively. A high reactivity of the $[Eu(L)_3]$ (L = dpdmg, dpamd, dpfamd) towards O_2 and S_2 was obtained from DFT studies, further underlining the suitability of these ligand motifs in precursors for vapor phase deposition fabrication methods.[1]

2:45pm **AF1-MoA-6 Novel Growth Inhibitor in Atomic Layer Deposition for Conformal Coverage on High Aspect Ratio Trenches***, **Kok Chew Tan**, J. Jung, C. Yeon, S. Lee, J. Kim, J. Nam, T. Park, Y. Park,* Soulbrain, Korea (Republic of)

The continuous miniaturization of semiconductor devices has triggered growing interests in new strategy for depositing conformal coatings on complex geometry which are critical for device reliability. Despite ALD being a mainstream technique for conformal coatings, features with increasing aspect ratio have rendered this conventional ALD increasingly challenging to achieve the desired step coverage.

Various approaches have been conducted to improve film conformality and film quality on high aspect ratio (HAR) trenches such as screening of molecules with potential chemistry as inhibitor and tuning of ALD process parameters. In this work, we have narrowed down our approach by successfully identifying molecules with suitable chemistry (alkyl-halides) that could act as growth inhibitor in the first pulse step of ALD. This inhibitor enables the control of inherent kinetics of gas transport within the trenches by reducing the surface reactive sites for precursors on the top region while allowing more precursors to diffuse deeper into the trenches, thus improving film conformality in high aspect ratio trenches. Besides growth inhibition, the selected inhibitor could function as film quality enhancer and could also be easily removed during reactant pulse step without contaminating the films.

By leveraging the selected inhibitor chemistry and ALD deposition characteristics, our approach has demonstrated significant improvement in TiN film conformality to 90% in HAR trench features, as determined by the ratio of bottom side film thickness to top side film thickness **[1]**. In terms of film resistivity, an observable 50% improvement was obtained owing partially to large decrease in Cl impurity as determined by SIMS depth profiles **[1]**. The introduction of inhibitor has also exhibited promising benefits in the ALD of high-*k* dielectric film, HfO_2. Improvement in HfO_2 film conformality to 97% in HAR trench features as well as significant improvement of 95% in leakage current due to enhancement in film quality were simultaneously observed **[2]**.

Based on these experimental evidences, our approach has been proven its promising potential as an innovative solution to address the challenges of depositing highly conformal films of excellent quality on high aspect ratio features such as DRAM trench capacitor and 3D NAND.

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3:00pm **AF1-MoA-7 Solution ALD: A Versatility Process for the Growth of Sulfides and Selenides***, **Maissa Barr**, B. Zhao, P. Von Grundherr,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; V. Koch,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; J. Charvot ,* University of Pardubice: Pardubice, CZ, Czechia*; M. Halik,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; F. Bureš,* University of Pardubice, Czechia*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

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

To illustrate this, we establish sALD procedures for depositing films of non oxides layers such as Pb-compound deposition, MOF, selenides and sulfides. Those examples highlight how ionic, polar, or high-molecular weight precursors that only exist in the condensed phase are now rendered amenable to being utilized in surface-controlled thin film formation by sALD for depositing materials that would otherwise be more difficult or more expensive to achieve by gALD or hazardous. The deposition was achieved on small (2 cm*1 cm) and large samples (up to 10 cm*10 cm). The ALD behavior has been shown. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition has been investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. Additionally, the nucleation is studied in function of chemical pretreatment to control the growth and allow selective deposition of SnS, SnSe and Sb_2Se_3.

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

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3:15pm **AF1-MoA-8 Flash-Lamp Enabled Atomic Layer Deposition***, Martin* ***Knaut****, Y. Cui, R. Deltschew, M. Albert, T. Mikolajick,* TU Dresden, Germany

Atomic layer deposition (ALD) processes are widely used in research and development as well as in various production environments. Nowadays, a variety of materials can be deposited using thermal and energy enhanced atomic layer deposition but there are limits that are mainly set by the properties of available precursors and the related processes. Besides the necessity of suitable precursors and chemical reactions to deposit a specific material, there are two major limitations: the thermal self-decomposition of precursor molecules which can be in conflict with the required process temperatures enabling desired film properties, and the typical temperature-related reactivity of precursors and co-reactants with substrate materials. These can affect the initial film growth and can lead to adhesion issues and unwanted interface layers, such as oxides formed by oxidizing agents used during the ALD process.
We developed a novel flash lamp enabled atomic layer deposition (FLE-ALD) process to address these limitations of common ALD processes. The process combines the self-limiting chemisorption of precursor molecules in the first half-cycle with a millisecond flash lamp anneal (FLA) during the second half-cycle. The heat applied during the second process step enables single-source ALD processes by inducing a thermal decomposition of chemisorbed molecules resulting in the desired film material.
This paper demonstrates the FLE-ALD approach for the deposition of oxide and nitride films in single-source processes combining metal organic precursor exposures with flashes of optical light with a duration in the millisecond range to heat a surface for a very short time and to decompose the chemisorbed molecules. The heat induced by the short FLA step is distributed into the substrate's bulk and the process chamber during the subsequent purging step, resulting in a constant substrate temperature and maintaining the self-limiting behavior of the precursor chemisorption.
The process development confirmed the FLE-ALD principle and the ALD typical self-limiting and constant growth per cycle by varying and characterizing process parameters like precursor dose, purge times, flash lamp energy, substrate temperature, and cycle number. Spectroscopic ellipsometry was used to measure the film thicknesses and to investigate the optical properties of the deposited films. The film composition was measured by X-ray photoelectron spectroscopy and scanning electron microscopy was used to analyze step coverage in high aspect ratio structures.

ALD Fundamentals
Room Auditorium - Session AF2-MoA
Simulation, Modeling, and Theory of ALD I

Moderators: Hannah Margavio, North Carolina State University, Bonggeun Shong, Hongik University

4:00pm **AF2-MoA-11 A User Experience Feedback on Numerical Simulation for CVD/ALD Precursor Design & Development***, Romain* ***Gaillac****,* Air Liquide **INVITED**

Molecular modelling has been a widely used tool in biochemistry or catalysis for decades. More recently, its application to CVD/ALD precursors has been suggested as a way to improve their design and development. We have explored its potential, especially through ab-initio molecular simulations.

In particular, we investigated the relevance of such simulations for the assessment of synthetic pathways and reactions occurring during Atomic Layer Deposition processes. We also assessed the interest of assisting analytical efforts with molecular simulations, for example for substance identification via spectra simulation.

Our work showed that molecular simulations are a useful tool for the development of new ALD precursors. They can be used to different degrees of accuracy to understand:

1. Intrinsic molecule stability, either isolated or in a condensed phase
2. Reaction thermodynamics and reaction paths
3. Surface adsorption/desorption and reactivity

However the predictive power remains to be improved, and at this point, it should be seen as a useful companion to experimental work. Effective collaboration between the synthetic chemists, ALD/CVD practitioners and molecular modeling theorists accelerates the acquisition of a chemical and mechanistic comprehension of ALD Precursors. Such learning can bring an acceleration to the design and development process.

4:30pm **AF2-MoA-13 From Monolayers to Crystalline Materials in ALD: Simulation and Comparison With Experiments***,* ***Angel Yanguas-Gil****, J. Elam,* Argonne National Laboratory

Controlling the microstructure of ALD materials is key for many different applications. In some cases, like gate dielectrics in microelectronics, the goal is to achieve materials with good interfaces and that lack grain boundaries to improve leakage and avoid the onset of breakdown. In other cases, applications require the growth of materials with good crystalline quality.

One of the key characteristics of ALD is that its growth conditions (low temperature and pulsed, self-limited nature) are far from those considered in traditional growth models, where the growth of crystalline materials is promoted by either large surface mobilities that allow relaxation or reversible processes close to thermodynamic equilibrium that tend to self-correct defects randomly occurring during growth. In this work, we present a model that explores the evolution of crystallinity and microstructure under self-limited and kinetically limited conditions characteristic of ALD. This model, based on a generalization of the Potts model, tracks the evolution of local coordination environments as a function of the number of ALD cycles, and differs from traditional approaches in the literature by considering the following assumptions: 1) microstructure relaxation takes place only through local rearrangement of atoms 2) relaxation is kinetically limited so that only transitions that lower the energy of the systems are allowed 3) growth takes place in a two-step process involving adsorption of a precursor and reaction with a co-reactant. When these are separated in time, the process is fully self-limited.

The simulation of the evolution of the medium range order, captured in the average size of locally ordered domains, agrees well with experimental results, both ex-situ and in-situ, obtained for a wide range of oxide materials including ZnO, Al_2O_3, and TiO_2. When the probability of local relaxation is high, the material grows from an amorphous interface into crystalline domains of increasing size, demonstrating that local relaxations are sufficient for crystallinity to emerge. This transition can take place in as few as 10 ALD cycles. On the other hand, if the relaxation is too slow or the growth rate is too large, the film reaches a metastable configuration composed of very small domains. These results open up the question of how to use ALD surface chemistry to promote crystallinity by enhancing such relaxation mechanisms. They can also explain some interesting phenomena observed in the ALD literature, such as explosive crystallization.

This research has been funded through Argonne's LDRD program.

4:45pm **AF2-MoA-14 What Is the Reactivity of a Precursor in ALD? - Simulation of Growth and Etch Rates***,* ***Simon D. Elliott****, A. Chew, Y. An,* Schrödinger, Inc.

In atomic level processing, the most important requirement is reactivity of a precursor towards deposition or etching of the target material; however, it is difficult to quantify reactivity. One possible experimental measure is the growth per cycle (ALD) or etch per cycle (ALE) under conditions where the chemistry is self-limiting. Experimentally measuring reactivity for all possible precursors and target materials is prohibitively expensive, necessitating alternative ways to explore the large design space.In this talk, we examine how to compute precursor reactivity with atomistic modeling.

We discuss long-standing models [1] that use density functional theory (DFT) to simulate ligand exchange in the precursor molecule itself as a measure of reactivity. Advantages of these models are conceptual simplicity, ease of computation and suitability for processing large sets of molecules [2]. Furthermore, these models can extend from oxides/nitrides to metals, approximate temperature effects and deliver formation energies.

However, more information about the multistep reaction mechanism is required to calculate the growth/etch rate of the process.We examine the thermodynamic basis that dictates how many reaction steps the precursor can undergo at the surface, i.e. the ‘extent’ of the reaction [3].The reaction extent can be converted into a growth/etch rate per cycle if additional information about ligand size and material density is calculated.We propose a high-throughput approach for computing surface reactions with DFT and hence quantifying the reaction extent and the growth per cycle.We then validate our approach against experimental data for commonly used precursors for the ALD of dielectrics.

Finally, we explore the capabilities of machine learning models (ML) to accurately predict the DFT reactivities using structure-property relationships. Since the computational time for running machine learning models is significantly lower than for DFT, an ML approach can enable thousands of ligands to be screened quickly.

These automated modeling approaches enable the quantification of precursor reactivity in terms of growth/etch rates, which will open new opportunities for *in silico* design and process understanding.

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5:00pm **AF2-MoA-15 Random Sequential Adsorption and the Consequences for the Growth-Per-Cycle of Atomic Layer Deposition Processes***, **Ilker Tezsevin**, S. Deijkers, M. Merkx, E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) processes are known to deposit a sub-monolayer of material per cycle due to (*i*) steric hindrance effects and/or (*ii*) limited availability of surface sites.[1, 2] Another contributing factor, which has not been addressed in detail, is that molecules arrive one by one at the surface and adsorb at random surface sites, such that the saturation coverage of precursor ligands substantially deviates from closed packing. In this work, the effect of the random sequential adsorption (RSA) mechanism on the saturation of precursor adsorption and hence on the growth per cycle (GPC) of ALD processes is investigated. By systematically varying the precursor radius and the precursor binding sites in the RSA simulations, the surface densities of the adsorbed precursor molecules are modelled. It is found that the random sequential adsorption of the precursor molecules results in a 25% to 68% lower surface density than the (unrealistic) reference case of closed packing of ligands. Moreover, RSA simulations are also used to model the growth-per-cycle values based on the precursor shape and size. Using this RSA model for metallocene precursor adsorption, GPC values of Co, Os, and Ru ALD processes are calculated as 0.28, 0.38 and 0.37 Å/cycle, in agreement with the experimental findings with accuracy of ± 0.08 Å/cycle. [3-5] Therefore, this work clearly demonstrates the importance of the random sequential adsorption mechanism on the ALD growth.

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5:15pm **AF2-MoA-16 Machine Learning Based Atomistic Modeling of ALD Processes***, J. Schneider, **Suresh Kondati Natarajan**, V. Arcisauskaite, U. Martinez,* Synopsys Denmark*; A. Blom,* Synopsys Inc.

Atomic layer deposition (ALD) of materials has been a key enabling technology for atomically fine-tuned manufacturing of semiconductor devices in the past two decades. As the future brings continued down-scaling of electronic devices, extreme fabrication limits require optimization of existing and development of new deposition setups for maximum process capability and yield, enabled by physical modeling with topography tools, such as Sentaurus Topography.

In this talk, we will show how machine learning (ML) based atomistic simulations of ALD processes can efficiently provide important parameters for topography simulations, which have been historically extracted from experiments. This multiscale modeling approach can be of particular importance when developing new deposition processes where experimental data are unavailable or expensive and time-consuming to obtain. We will demonstrate how to efficiently obtain ALD parameters such as sticking coefficient and maximum precursor coverage by simulating the $HfCl_4$ precursor pulse in the ALD of HfO_2.

ALD atomistic simulations can be computationally very demanding or even unmanageable if performed using *ab initio* density functional theory (DFT) molecular dynamics (MD), whereas computationally cheaper conventional Force Fields are often not available and require a long and error-prone process to be developed, as in the case for $HfCl_4$-HfO_2. This can be overcome by generating and using ML based interatomic potentials (MLIPs). In this work, we efficiently developed and used moment tensor potentials (MTPs), which provide high accuracy with lower computational cost when compared to other MLIPs [1,2]. MTP was trained using reference data from DFT simulations to reproduce *ab initio* quality potential energy surface of the $HfCl_4$-HfO_2 system. MD simulations with such trained MTPs give us DFT quality MD trajectories at a significantly (100x) reduced computational effort. Automated MTP training and MD simulations were performed using the QuantumATK software [3,4] developed by Synopsys.

MD simulations of $HfCl_4$ molecules impacting the HfO_2 (111) substrate reveal that Hf atoms bind to O atoms on the surface as expected, with binding energies being consistent with DFT results. Finally, we show that the sticking coefficient of the precursor decreases as its surface coverage increases and becomes 0 after attaining a maximum coverage at 0.3 monolayers.

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[3] S. Smidstrup et al. , J. Phys.: Conden. Matter 32, 015901 (2019).
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5:30pm **AF2-MoA-17 Modelling Ruthenium Deposition in Atomic Layer Deposition of Ru-doped TaN***, **Rita Mullins**, M. Nolan,* Tyndall National Institute, Ireland

The downscaling of semiconductor devices has led to critical issues with the widely used Cu interconnect such as diffusion into the substrate dielectric layer. A Ru-doped TaN surface is a promising combined barrier and liner material that has the liner properties of Ru and barrier properties of TaN. Ru has good adhesion strength with Cu, high thermal stability and can promote direct electrodeposition of Cu. A previous first principles density functional theory study found that Ru doping of TaN produces nucleation sites for Cu growth and promotes formation of conducting Cu films.

Atomic layer deposition (ALD) allows the fabrication of ultra-thin films for a wide range of applications and offers excellent conformity and thickness control. ALD is a self-limiting film growing process distinguished by exposure to alternating precursors that are introduced sequentially. Similar to thermal ALD, plasma-enhanced ALD (PE-ALD) provides potential advantages such as improved film purity and the facility for deposition at reduced substrate temperatures. To avoid oxygen contamination in PE-ALD process for metals, non-oxidative reactants are chosen. Furthermore, PE-ALD of Ru using oxygen plasma can lead to lower growth or even the absence of growth due to oxygen plasma competitive etching of Ru. Replacing oxygen plasma with NH_3 plasma leads to the formation of smooth Ru films.

In this contribution, the chemistry of NH_x (x = 1,2) surface terminations of TaN and their reaction with Ru precursors is studied using first principles density functional theory (DFT) using the $RuCp_2$ precursor. NH_x-terminations of TaN for the post plasma surface are studied to test their coverage and stability. The TaN surface consists of 24 N (1 ML) and 24 Ta (1 ML) sites that could be H/H_2 and NH/NH_2 terminated respectively. Stable coverages of 1 ML H and 0.5 ML H/0.5 ML H_2 terminated were found for the 24 N sites. For the 24 Ta sites, stable coverages of 0.04 ML NH_2/0.46 ML NH and 0.67 ML NH_2 terminated were found. The adsorption of precursor $RuCp_2$ to the stable NH_x terminated TaN surfaces is then examined. The Cp ligands are lost through hydrogen transfer from the NH_x-terminated surface to the Cp ligand in this mechanism. No spontaneous hydrogen transfer was observed on any of the NH_x-terminated TaN upon adsorption of $RuCp_2$. Therefore the hydrogen transfer step must overcome activation barriers which are computed using the nudged elastic band method.

ALD Fundamentals
Room Van Eyck - Session AF3-MoA
Plasma Enhanced ALD

Moderators: Sumit Agarwal, Colorado School of Mines, Andreas Werbrouck, Ghent University, Belgium

1:30pm **AF3-MoA-1 Revisited Thermal and Plasma Enhanced Atomic Layer Deposition Processes of Metal Nitrides***, **Elisabeth Blanquet,*** SIMaP, CNRS , University Grenoble Alpes, France*; A. Mantoux,* SIMaP, University Grenoble Alpes, France*; F. Mercier,* SIMaP, CNRS, University Grenoble Alpes, France*; R. Boichot,* SIMAP, Grenoble-INP, University Grenoble Alpes, France*; I. Nuta,* SIMAP, CNRS, University Grenoble Alpes, France*; C. Jimenez,* LMGP, CNRS, University Grenoble Alpes, France **INVITED**

Metal nitrides films stand out as candidates for many strategic industrial applications as they exhibit superior functional properties such as mechanical, electrical and thermal properties. Complementary chemical vapor deposition techniques from High Temperature Chemical Vapor Deposition (HTCVD) to Thermal and Plasma Enhanced Atomic Layer Deposition (T-ALD and PEALD) have been investigated to fabricate metal nitrides thin films. Coupling or combining these techniques might open new opportunities. In each case, one of the major challenges is the synthesis of high quality, pure (with no oxygen contamination) material. Among ALD developments, efforts have been focused on the exploration of thermal stabilities of different precursor molecules, chemical reactions as well as growth processes sequences and conditions.

In this presentation, the examples of various metal nitride deposition process development with special focus on Aluminum nitride will be presented. AlN is a multifunctional material, which has been widely investigated for many potential applications in recent years, due to its high melting point, excellent thermal conductivity and good chemical stability and behavior towards oxidization and abrasion with respect to other nitrides. It is a semiconductor material with a wide bandgap, offering transparency even in the UV region. Moreover, its oxidation rate is low at temperatures below 1100°C. AlN films are attractive for applications in energy, aeronautics, electronic or optoelectronic devices. For instance, thin films are investigated in piezoelectric based applications, as passivating and protective coatings for metallic architectures, as AlN substrate in high power applications.

We report on the optimizing routes and strategies via coupling deposition processes to obtain the best film properties on various systems.

2:00pm **AF3-MoA-3 Plasma-Enhanced Low-Temperature ALD Process for Molybdenum Oxide Thin Films and Its Evaluation as Hydrogen Gas Sensors***, **Jan-Lucas Wree**, J. Klimars,* Ruhr University Bochum, Germany*; N. Saliha,* Heinrich-Heine University Düsseldorf, Germany*; D. Rogalla,* Ruhr University Bochum, Germany*; K. Schierbaum,* Heinrich-Heine University Düsseldorf, Germany*; A. Devi,* Ruhr University Bochum, Germany

The versatile properties of molybdenum oxide strongly depend on the structural features and in particular on its crystallinity, composition and morphology. This makes it an interesting material class for a variety of applications, i.e., (opto)electronics, (photo)catalysis and gas sensors. Moreover, the performance of these applications is significantly enhanced by the implementation of the active material in thin film form. Therefore, the development of atomic layer deposition (ALD) processes for the fabrication of nanostructured molybdenum oxide thin films has grown steadily in the recent years. As a consequence, the demand for suitable molybdenum precursors with improved physico-chemical properties is rising as the library for appropriate molybdenum precursors is rather small.

In this study, molybdenum oxide thin films were deposited using a new plasma-enhanced ALD (PEALD) process employing the molybdenum precursor $Mo[(N^{t}Bu)_2(^{t}Bu_2DAD)]$, recently developed in our group, and oxygen plasma. The process yielded a growth rate of 0.75 Å/cycle on Si(100), which is in the range of other PEALD processes reported for molybdenum oxide. Furthermore, the linear dependence of the thickness on the number of cycles was confirmed within a temperature window between 100°C and 240°C. X-ray diffraction (XRD) patterns show that on the lower end of the temperature window the films appear to be amorphous while crystallization starts at the higher end (240°C), yielding nanocrystalline β-MoO_3 thin films. Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA) and X-ray photoelectron spectroscopy (XPS) analyses revealed the formation of pure films, while SEM analysis showed the smooth morphology of the films with crystallite formation at higher deposition temperatures. Furthermore, sensor substrates were coated with molybdenum oxide to investigate the resistive hydrogen sensitivity of the thin films with respect to their morphology. This study demonstrates that the recently developed molybdenum precursor is suitable for the utilization in ALD applications. The resistive response of the deposited MoO_x thin films towards hydrogen gas reveals the potential of this material for thin film hydrogen gas sensors. Moreover, the overall quality of the films makes it also promising for implementation in other applications such as catalysis and optoelectronics.

2:15pm **AF3-MoA-4 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Crystalline Tin Disulfide Thin Films***, **Femi Mathew**, N. Poonkottil, R. Karuparambil Ramachandran, B. Zhao, Z. Hens, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Among the layered metal dichalcogenide materials, semiconducting tin disulfide (SnS_2) is a potent candidate for photocatalysis, field-effect transistors, lithium-ion batteries, and gas sensing applications. Hence, there is a demand for a scalable technique to uniformly and conformally deposit SnS_2 thin films, preferably at low temperatures. Here, we present a plasma-enhanced atomic layer deposition (PE-ALD) technique to deposit crystalline SnS_2 using tetrakis(dimethylamino)tin (TDMASn) precursor and H_2S/Ar plasma at temperatures as low as 80°C.

TDMASn precursor was previously combined with H_2S to deposit tin sulfides via thermal ALD.[1] We employed H_2S plasma as the reactant inspired by previous reports demonstrating a significant effect of using plasma on the ALD growth characteristics and material properties.[2] The new PE-ALD process is self-limiting with a growth per cycle of 0.45-0.15 Å/cycle in a temperature range of 80 –180 °C. **(Fig. 1)** In contrast to the thermal ALD process which deposits amorphous SnS_2 thin films at 80°C and a mixture of SnS and SnS_2 phases at 180°C, crystalline SnS_2 thin films are deposited with the PE-ALD process in the temperature range of 80-180°C.**(Fig. 2)** Moreover, scanning electron microscopy analysis shows an evolution in thin-film morphology from grain-like structures with size in the range of 30-50 nm to out-of-plane oriented structures for SnS_2 deposited by the PE-ALD process at 80°C and 180°C, respectively. **(Fig. 3)** Optical transmission measurements detected an indirect bandgap in the range of 2.1-2.3eV in all the as-deposited SnS_2 thin films. **(Fig. 4)**

SnS_2 nanostructures with different morphologies have been previously investigated as anode materials in lithium-ion batteries to counter the problems of poor capacity retention associated with significant volume changes during cycling. Thus, we compared the electrochemical performance of SnS_2 thin films with three different morphologies as anode material in Lithium-ion batteries. The SnS_2 thin films with out-of-plane orientation structures exhibit better cycling stability with a capacity retention of 77% in contrast to the amorphous films which show 34% capacity retention after 100 cycles. **(Fig. 5)** We assume these out-of-plane orientation sites facilitate the diffusion of Li^+ ions thus limiting the pulverization and retaining the capacity.

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2:30pm **AF3-MoA-5 Leveraging Non-Saturated Oxidation Conditions in Plasma-Enhanced Atomic Layer Deposition for Tuning Functional Properties of CoO_x Catalyst Layers***, **Matthias Kuhl**, A. Henning, L. Haller, L. Wagner, C. Jiang, V. Streibel, I. Sharp, J. Eichhorn,* Technical University Munich, Germany

Electrocatalysts often suffer from poor stability under operating conditions due to (electro)chemical susceptibilities and/or poor adhesion to the support structure. For the realization of highly active and stable catalytic layers, catalyst-support integration and interface engineering play important roles. Interface engineering is also decisive for the integration of electrocatalysts with semiconductor light absorbers for solar-to-chemical energy conversion. For designing surfaces and interface layers of energy conversion devices, plasma-enhanced atomic layer deposition (PE-ALD) has emerged as a powerful method. These processes are typically developed with the aim of ensuring saturated surface oxidation reactions. However, exploring less aggressive process parameters opens new opportunities to precisely tailor the functional properties of active catalysts.

Here, we elucidated non-saturated oxidation of cobaltocene precursor by varying the plasma exposure time and plasma power to precisely control structural, mechanical, and optical properties of biphasic CoO_x thin films, thereby tailoring their catalytic activities and chemical stabilities.[1] Short pulses and low plasma power facilitate the formation of porous, unstable $Co(OH)_2$ layers with high electrochemical activity, while long pulses and high power yield stable, inactive Co_3O_4 layers. The best combination of stability and activity is observed for intermediate plasma exposure times leading to the formation of biphasic films consisting of a $Co(OH)_2$ surface and Co_3O_4 interface layer. The underlying reason for the formation of a porous $Co(OH)_2$ surface layers is the incomplete decomposition of the precursor at either short pulse durations or low plasma power, which also leads the incorporation of carbon impurities. The corresponding change in the chemical composition is reflected in the respective growth chemistry, which is characterized by reduced precursor adsorption and changes in the growth per cycle. The gained mechanistic insights were applied in a two-step growth process to intentionally engineer bilayer films consisting of a stable Co_3O_4 interface layer with a catalytic $Co(OH)_2$ surface exhibiting improved electrochemical performance without sacrificing chemical stability. This work highlights that unsaturated oxidation allows access to different material phases with tailored properties for engineering active catalysts and their interfaces.

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2:45pm **AF3-MoA-6 Low-temperature HfO_2/SiO_2 Gate Stacked Film Grown by Neutral Beam Enhanced Atomic Layer Deposition***, **Daisuke Ohori**,* Tohoku University, Japan*; B. Ge,* Tohoku University, China*; Y. Chen,* National Yang Ming Chiao Tung University, Taiwan*; T. Ozaki,* Tohoku University, Japan*; K. Endo,* National Institute of Advanced Industrial Science and Technology, Japan*; Y. Li, J. Tarng,* National Yang Ming Chiao Tung University, Taiwan*; S. Samukawa,* Tohoku University, Japan

Fabrication of the high-quality insulating film with reduction of the thermal budget in a process is required for the metal-oxide-semiconductor (MOS) transistor fabrication with next-generation semiconductor material such as Ge and SiGe. Hafnium dioxide (HfO_2) is one of the promising candidate materials due to its high dielectric constant (high-k-value), thermal stability, and a high-quality interface between HfO_2 and SiO_2 for reduction of the gate leakage current with miniaturization of fabrication scale. To deposit a high-quality gate dielectric film on a high aspect ratio channel, the atomic layer deposition (ALD) method has been adopted with high coverage and thickness control. We have already successfully deposited high-quality SiO_2 films using defect-free neutral beam enhanced ALD (NBEALD) at low substrate temperature (30 ºC).In this study, we demonstrated a high-quality amorphous $HfO_2/SiO_2/Si$ structure using low-temperature NBEALD.

The NBEALD was carried out in a large chamber for an 8-inch diameter. A precursor and carrier gases were Tetrakis(ethylmethylamino)hafnium (TEMAH) and Ar, respectively. The Si(100) substrate was cleaned with sulfuric acid hydrolysis (4 sulfuric acid:1 hydrogen peroxide) and 1% hydrofluoric acid, and then high-quality SiO_2 with a thickness of 1.6 nm could be initially formed after oxygen NB irradiation. After that, samples were grown under the following ALD growth conditions: gas supply (5 sec), purge (5 sec), oxygen NB irradiation (20 sec), oxygen gas purge (5 sec). Oxygen plasma for oxygen neutral beam was discharged at 1300 W, while the bias was not applied, and the stage temperature was at the room temperature, 30 ºC. Different thicknesses of HfO_2 films were deposited by using 50, 100, 150, and 200 cycles to evaluate the film characteristics. The surface roughness and crystalline state of deposited HfO_2 films were evaluated by atomic force microscopy (AFM) X-ray diffraction (XRD) measurements. The surface roughness increased from 0.3 to 1.1 nm with increasing growth cycle. XRD results were measured by the θ-2θ scan. Any typical diffraction peaks were not observed for all the samples. Therefore, we could successfully form high uniformity amorphous HfO_2/SiO_2 thin films even at low temperatures in an in-situ environment. It is suggested that this technique can contribute to the development of the MOS transistor fabrication process with a small heat budget in the future. Finally, we can discuss the electrical characteristics of nano-devices.

3:00pm **AF3-MoA-7 Effect of O_2 Plasma Exposure Time During Atomic Layer Deposition of Amorphous Gallium Oxide***, **Florian Maudet**,* Helmholtz Zentrum Berlin, Germany*; H. Kröncke, S. Banerjee, K. Nair, C. Van Dijck,* Helmholtz-Zentrum Berlin, Germany*; S. Wiesner, J. Albert, V. Deshpande,* Helmholtz Zentrum Berlin, Germany*; C. Dubourdieu,* Helmholtz-Zentrum Berlin, Germany

Crystalline gallium oxide is an attractive ultrawide bandgapsemiconductor, which can be intentionally donor-doped with a large range of accessible electron carrier densities. Amorphous gallium oxide, on the other hand, has been comparatively less studied although it can demonstrate benefit for applications in photovoltaics and electronics. We have investigated the ability to self-doped amorphous gallium oxide thin films grown by atomic layer deposition (ALD) to tune their electrical properties from insulating to semiconducting.

Amorphous gallium oxide (GaOx) thin films were grown at 200 °C by plasma-enhanced ALD on (100) silicon substrates from trimethylgallium $Ga(CH_3)_3$ precursor and O_2 plasma. The effect of O_2 plasma exposure time during ALD cycles on the optical and electrical properties was investigated with the help of *in situ* and *ex situ* spectroscopic ellipsometry and electrical characterization. The O_2 plasma exposure time was varied from 1s up to 30 s. We will first discuss the regrowth of the interfacial SiO_x during the plasma-enhanced ALD. We will then present the effect of the O_2 plasma exposure time on the optical index, extinction coefficient, dielectric constant and leakage currents. An increase in the O_2 plasma exposure time during each ALD cycle up to 30 s - well beyond the time needed to reach a constant growth per cycle - leads to a drastic decrease in the leakage current density by more than five orders of magnitude (for 30 nm films). Interestingly, a concomitant increase in the dielectric constant is observed, reaching a value of $\varepsilon_r \sim 14.2$, larger than that of the single crystalline β-Ga_2O_3. At O_2 plasma exposure times below 8 s, the presence of oxygen vacancies is evidenced with an increasing amount as the exposure time decreases. Finally, we will discuss the information gained from the analyses of *in situ* spectroscopic ellipsometry in the very first stages of the growth (first 10 cycles). A method was developed to unambiguously determine the thickness and optical properties of the growing oxide. We will discuss the change in thickness as a function of time for each of the four steps of the ALD cycles. The change in optical properties, determined after each step within one cycle and for all cycles, give information on the evolution of the film until a “bulk-like” gallium oxide film is reached.

Our study highlights the crucial role of O_2 plasma exposure time during PEALD of amorphous gallium oxide films in the control and tuning of their electrical properties. The ability to self-doped this material can be used to design e.g. semiconducting a-GaO_x channel field-effect device.

ALD Fundamentals
Room Van Eyck - Session AF4-MoA
Surface Science

Moderators: Annelies Delabie, IMEC, Virginia Wheeler, U.S. Naval Research Laboratory

4:15pm **AF4-MoA-12 Thickness Matters: Sintering Inhibition of Pt Nanoparticle Catalysts via Sequential Control of MgO Overcoats***, **Zhiwei Zhang**, M. Filez, M. Minjauw, J. Li, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Overcoating of metal nanoparticles (NPs) to modulate the performance and thermal stability of catalysts has been proven as an effective method.[1] However, most studies focus on the catalytic effects that overcoats bring to the table, while researching their deposition processes is rare, but crucial to tailoring their properties. Here, atomic layer deposition (ALD) of magnesium oxide (MgO) overcoating on platinum (Pt) NPs is developed and investigated. The thickness of the MgO overcoat is precisely controlled by ALD. The prime function of the overcoat is to prevent rapid NP coarsening during the catalyst lifetime, here simulated by high-temperature annealing. During annealing, the NP properties are monitored in real-time by in-situ grazing incidence small angle X-ray scattering (GISAXS)[2,3].

$Mg(EtCp)_2$ and H_2O are used as Mg precursor and reactant of the MgO ALD process, respectively, while both 150 ℃ and 200 ℃ deposition temperatures were compared. The ALD process of MgO is initially more selective to Pt than to SiO_2 when using bare SiO_2 and sputtered Pt reference substrates. Via *ex-situ* XPS after MgO ALD on Pt NP-decorated SiO_2, the evolution of the relative Mg intensity as the function of the number of ALD cycles is shown (Figure 1). It is found that MgO shows a higher growth per cycle at 150 ℃ compared to 200 ℃, consistent with previous work. [4] In addition, during the first cycles, MgO mainly covers the Pt NPs, since the Pt signal decreases while the Si contribution remains constant. During the subsequent cycles, the Si intensity also decreases in XPS, suggesting MgO is now grown on the SiO_2.

In-situ GISAXS during annealing (from 25 ℃ to 800 ℃) is adopted to study the influence of MgO overcoating on the Pt NP coarsening behavior. A clear sintering delay is observed for both 150 ℃ and 200 ℃ sample sets with increasing number of MgO ALD cycles. However, the very first cycles (e.g. 1-3) do not contribute too much to the anti-sintering behavior which suggests that decorating the Pt NPs with MgO alone is insufficient for catalyst protection (Figure 2a). The sintering onset temperature is significantly delayed as the number of MgO cycles increases beyond the first cycles, which indicates the NPs thermal stability is mainly enhanced once MgO coats the SiO_2 substrate. This trend is generally applicable for both deposition temperatures, clearly showing a critical amount of MgO is necessary to prevent catalyst coarsening (Figure 2b).

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4:30pm **AF4-MoA-13 Route to Low Temperature Area-Selective Atomic Layer Deposition of Ni***, **Himamshu Nallan**, X. Yang, J. Ekerdt,* The University of Texas at Austin

Nickel and nickel oxide are utilized within various device heterostructures for chemical sensing, solar cells, batteries, etc. Recently, the increasing popularity of flexible electronics to enable ubiquitous as well as large-area consumer electronics such as next-generation displays and sensors has driven interest in the development of low temperature fabrication processes for the integration of inorganic devices with polymeric substrates. Given the thermal constraints of the substrate as well as the desire for high-throughput and large-area scalability, ALD is a suitable fabrication method. Here we investigate the low temperature area-selective ALD (AS-ALD) of Ni by reduction of preformed NiO. Area-selective deposition of NiO is performed at 100 °C using bis(N,N'-di-t-butylacetamidinato)nickel(II) and water on SiO_2. NiO grows two dimensionally and without nucleation delay on oxide substrates; pre-patterned sp^3 carbon-rich resists inhibit the nucleation of NiO. In this way, first, carbon-free NiO may be patterned. Subsequent thermal reduction of NiO to Ni was investigated using H_2 (50 mTorr) and thermally-generated H atoms ($2.5x10^{-6}$ Torr chamber pressure). Due to relatively high surface energy, Ni films undergo dewetting at elevated temperatures when solid-state transport is enabled. Reduction of NiO to Ni is demonstrated at 100 °C and below using atomic hydrogen. *In-situ* x-ray photoelectron spectroscopy is used to determine oxidation state and *ex-situ* x-ray reflectivity and atomic force microscopy are used to probe the film thickness and surface morphology, respectively.

4:45pm **AF4-MoA-14 Hydrogen Plasma-Assisted Atomic Layer Deposition of sub-Nanometer AlO_x for Low-Impedance Contacts to GaN***, **Maximilian Christis**, A. Henning,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany*; J. Bartl,* Walter Schottky Institute, Physics Department, and WACKER-Chair for Macromolecular Chemistry, Department of Chemistry, Technical University of Munich, Germany*; A. Zeidler,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany*; B. Rieger,* Department of Chemistry, WACKER-Chair for Macromolecular Chemistry, Technical University of Munich, Germany*; M. Stutzmann, I. Sharp,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany

To achieve low-impedance tunneling contacts, wet-chemical pretreatments are usually required to prepare the semiconductor surface by removing the native oxide layer. Following this step, it is critical to produce continuous sub-nanometer thin coatings, which are challenging to achieve by atomic layer deposition (ALD) due to surface inhomogeneities and precursor steric interactions that result in island growth during film nucleation. Here, we report a novel atomic layer deposition process that alleviates the need for wet chemical etching and achieves full encapsulation of *c*-plane gallium nitride (GaN) with an ultimately thin (~3 Å) AlO_x monolayer, which is enabled by the partial transformation of the GaN surface oxide into AlO_x. This is accomplished using repeated cycles of trimethyl aluminum (TMA) and hydrogen (H_2) plasma exposure in a commercial plasma-enhanced ALD reactor (Ultratech Fiji G2). The introduction of ultra-thin AlO_x significantly modifies the physical and chemical properties of the surface, decreasing the work function and introducing new chemical reactivity [1][2]. Electrochemical cyclic voltammetry (CV) measurements show that the ultra-thin film poses a significantly smaller tunneling barrier to charge carrier transport than the thinnest homogenous AlO_x coatings achievable with the conventional TMA/H_2O ALD process.

Depending on the H_2 plasma parameters, the GaO_x surface oxide on GaN can be fully converted into AlO_x, reducing surface band bending and Schottky barrier height at the n-GaN/metal interface. Titanium-contacted n-doped GaN with an ultra-thin interfacial AlO_x layer shows a low contact resistance value and Ohmic behavior even before annealing. Unlike conventional Ohmic contacts to n-type GaN, this annealing-free contact allows for the integration of GaN with other semiconductors such as Si, for which the thermal budget is relatively low (≤ 400 °C). Given the high reactivity of TMA with surface oxides, the presented monolayer AlO_x deposition scheme likely can be extended to other dielectrics and III-V-based semiconductors, with significant relevance to applications in optoelectronics, chemical sensing, and (photo)electrocatalysis.

[1] A. Henning, J. D. Bartl, A. Zeidler, S. Qian, O. Bienek, C.-M. Jiang, C. Paulus, B. Rieger, M. Stutzmann, I. D. Sharp, *Adv. Funct. Mater.* 2021, 31, (33), 2101441.

[2] J. D. Bartl, C. Thomas, A. Henning, M. F. Ober, G. Savasci, B. Yazdanshenas, P. S. Deimel, E. Magnano, F. Bondino, P. Zeller, L. Gregoratti, M. Amati, C. Paulus, F. Allegretti, A. Cattani-Scholz, J. V. Barth, C. Ochsenfeld, B. Nickel, I. D. Sharp, M. Stutzmann, B. Rieger, *J. Am. Chem. Soc.* 2021, 143, (46), 19505–19516.

5:00pm **AF4-MoA-15 Tunable Ti^{3+}-Mediated Charge Carrier Dynamics of Atomic Layer Deposition Grown Amorphous TiO_2***, **Jesse Saari**, H. Ali-Löytty,* Surface Science Group, Tampere University, Finland*; M. Kauppinen,* Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Sweden*; M. Hannula,* Surface Science Group, Tampere University, Finland*; R. Khan,* Photonic Compounds and Nanomaterials group, Tampere University, Finland*; K. Lahtonen,* Faculty of Engineering and Natural Sciences, Tampere University, Finland*; L. Palmolahti,* Surface Science Group, Tampere University, Finland*; A. Tukiainen,* Faculty of Engineering and Natural Sciences, Tampere University, Finland*; H. Grönbeck,* Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Sweden*; N. Tkachenko,* Photonic Compounds and Nanomaterials group, Tampere University, Finland*; M. Valden,* Surface Science Group, Tampere University, Finland

Amorphous titania (am.-TiO_2) has gained broad interest in the field of photocatalysis due to its exceptional disorder-mediated optical and electrical properties compared to crystalline TiO_2 [1–3]. For instance, Ti^{3+} defects within am-TiO_2 can enable essential charge carrier transport through a protective am-TiO_2 photoelectrode coating in photoelectrochemical (PEC) cells [1], and Ti^{3+}-mediated visible light active amorphous "black" titania is regarded as a potential material for photocatalytic applications [2]. Atomic layer deposition (ALD) allows for tuning the defect composition and structure of am.-TiO_2 thin films via precursor choices and process parameters. Recent progress in computational analysis of am.-TiO_2 [3] has provided means to accurately correlate experimental insights with theoretical models, which can be utilized to tailor am.-TiO_2 coatings with desired properties.

This work examines how intrinsic titanium and nitrogen defects in am.-TiO_2 can be tailored in a controlled and elegant manner via tuning the ALD growth temperature between 100–200 °C when using tetrakis(dimethylamido)titanium(IV) (TDMAT) and water (H_2O) as the precursors. X-ray photoelectron spectroscopy (XPS) analysis and density functional theory (DFT) calculations allowed us to identify structural disorder-induced penta- and heptacoordinated Ti^{4+} ions ($Ti_{5/7c}^{4+}$), which are interrelated to the formation of Ti^{3+} defects in am.-TiO_2 without releasing oxygen, i.e., simultaneous formation of oxygen vacancies and interstitial peroxo species leading to defective but stoichiometric am.-TiO_2. When changing the ALD growth temperature from 100 °C to 200 °C, increase in Ti^{3+} concentration results in "black" TiO_2 and electrical conductivity via polaron hopping mechanism. Furthermore, transient absorption spectroscopy (TAS) shows that the high concentration of Ti^{3+} defects in "black" TiO_2 increases the carrier lifetime to the nanosecond time domain comparable to crystalline low-defect TiO_2. These insights into the formation of Ti^{3+} defects in am.-TiO_2 and into tuning the charge transport properties of ALD grown am.-TiO_2 are beneficial in wide range of applications, such as protective photoelectrode coatings.

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5:15pm **AF4-MoA-16 Temperature-Time-Thickness (Ttt) Topography Maps: A Parameter Space Visualization Approach for ALD Processes***,* ***Parag Banerjee****, N. Berriel, U. Kumar, C. Feit,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; K. Basu,* University of Texas at Dallas, USA*; S. Seal,* University of Central Florida

ALD processes are developed and optimized in a limited, 1D process parameter space. The establishment of a steady growth rate within a temperature 'window' occurs via a series of experiments, where the independent variable – temperature is varied while holding pulse time constant. Similarly, saturation curves are obtained by varying the independent variable - pulse time (*i.e.,* dose) of the precursors while holding temperature constant. The demonstration of i) a viable temperature window and, ii) saturation curves constitute the establishment of an ALD process. The limitation of these approaches is that process parameter interdependencies cannot be studied. Thus, it is not possible to study the impact of temperature on dose saturation and *vice versa*. We hypothesize that these interdependencies hold a rich source of undiscovered ALD operation regimes and can lead to efficient process development, robust control and optimization outcomes.

In this talk, we present temperature-time-thickness (TTT) topography maps of ALD processes generated using *in situ* spectroscopic ellipsometry. Based on the methodology shown by our group recently[1], we demonstrate TTTof several ALD processes including, Al_2O_3, ZnO, CeO_2 and TiO_2 and plasma enhanced ALD (PEALD) of TiO_2. The visualization of these processes in 3D is through a combination of temperature and dose times for thermal ALD processes and as temperature and plasma power for PEALD processes. Saturation regimes of growth rates are observed as 2D surfaces i.e., plateaus and valleys. Precursor adsorption kinetics and thermodynamic parameters are extracted assuming ideal Langmuir adsorption behavior. We propose that a comprehensive database of TTT topographic maps can be used for deeper understanding of processes and to enable robust process control and optimization outcomes.

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5:30pm **AF4-MoA-17 *in situ* TEM Study to Unravel Dynamic Processes during the Synthesis of Ultrathin Crystalline ALD Nanotubes***,* ***Lilian Vogl****, P. Schweizer, L. Pethö, A. Sharma,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; E. Spiecker,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

By using Atomic Layer Deposition (ALD), amorphous nanotubes can be successfully made of various metal oxides. However, the creation of **high quality crystalline nanotubes** for example made of sapphire is still a challenging process. To control the crystal structure of ALD based systems, it is indispensable to use microscopy techniques to understand the dynamic processes occurring on atomic scale. In this study, we present a universal approach to create **ultrathin crystalline** ALD nanotubes by using a comprehensive annealing process of specific core-shell nanowires. In combination with correlative *ex situ* observations, ***in situ* TEM** heating experiments unravel diffusion processes going on at small scales and give insights about temperature induced changes of the metal-ALD interface. Heating core-shell nanowires (e.g. Cu/ALD-Al_2O_3) at temperatures below 1000°C lead to the creation of hollowed amorphous ALD nanotubes. While the ALD framework is stable, the **diffusion of the metallic core material** is activated. The conformal ALD shell acts as barrier for the material diffusion and forces the core to continuous diffusion towards the cracked end of the nanowire (Figure 1a). As a first heat-induced phenomenon we observe the creation of voids, which is caused by vacancy agglomeration. Vacancies are induced during the growth process of the metal nanowires at elevated temperatures. However, heating for longer time, the voids and therefore the vacancies get compensated. The thermal activation for the material diffusion can be observed *in situ* with **high resolution** imaging (figure 1b). The energy barrier to release an atom from the bonded state can be overcome by heat treatment and the released atoms diffuse within the inner cavity of the ALD tube. The time for releasing atoms scales directly with the temperature (figure 1c). By holding the temperature, no core material is left within the ALD framework and an amorphous nanotube is created. The nanotubes have a **high aspect- ratio** with lengths up to 40 µm and a wall thickness of 4 nm. At temperatures above 1000°C, a **phase transition** is induced and a crystalline dense microstructure (κ-Al_2O_3) is achieved (figure 1d).

This type of ultrathin nanotubes shows promising optical and mechanical properties and are the ideal candidate for further functionalization processes.

ALD Fundamentals
Room Arteveldeforum & Pedro de Gante - Session AF-MoP
ALD Fundamentals Poster Session

AF-MoP-1 Unearthing Ruthenium Diazadienyls as Precursors for the ALD of Ru Thin Films: Precursor Assessment and ALD Process Development*,* ***David Zanders**, J. Obenlüneschloss,* Ruhr University Bochum, Germany*; M. Gock,* Heraeus , Germany*; A. Devi,* Ruhr University Bochum, Germany

Ruthenium thin films are garnering significant interest as next-generation interconnects to replace Cu in future nanoelectronic devices. Especially in the back end of line (BEOL) and middle of line (MOL), ongoing scale down towards 2 nm and beyond has motivated alternative metallization approaches such as semi-damascene in which Ru outperforms Cu and Co notably.[1,2]One deposition technique most suitable to provide thin films for challenging interconnect device architectures is ALD.[3] A paramount factor in each ALD process is the choice of precursors and their chemistry that governs layer formation and material quality. A review of the current ALD processes for Ru thin films shows that a considerable number of often closely related precursors with their individual advantages and drawbacks have been employed.[4] Hitherto, none of them could fully satisfy academic and industrial demands alike.

This presentation describes the synthesis and detailed characterization of an alternative Ru precursor class: Ru diazadienyl cymenes [Ru(DAD)(Cym)] and their potential for CVD and ALD applications. Two examples, Ru(tBuDAD)(Cym) and Ru(iPrDAD)(Cym) (Figure 1) were obtained in high yields in a one-pot synthesis and thoroughly assessed in terms of purity (NMR, EA) and structure (SC-XRD). The structures were reproduced by DFT studies and subjected to bond dissociation analysis which rendered them appreciably stable. Thermal stability upon evaporation was evaluated in more detail alongside overall evaporation behaviour in thermogravimetric analyses (TGA) (Figure 2). Vapor pressures of the two complexes were derived and compared to the most often used $Ru(EtCp)_2$. Especially Ru(iPrDAD)(Cym) showed appreciable volatilization and deemed competitive towards the reference compounds.

Thus, Ru(iPrDAD)(Cym) was employed as precursor in a PEALD process with O_2 plasma. Preliminary results demonstrated the growth of thin, pinhole-free, low roughness films on Si(100) at temperatures as low as 120 °C (Figure 3). A full process study investigating typical ALD growth characteristics in terms of saturation, temperature dependency of film growth and thickness scalability was carried out to assess the ALD behaviour. Complementarily, AFM, RBS/NRA and XPS as well as resistivity measurements were performed.

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AF-MoP-2 Towards Greener ALD Processes: The Precursor Chemistry Is Key*,* ***Matthieu Weber**,* LMGP - Grenoble INP , France*; O. Graniel, D. Muñoz-Rojas,* LMGP - Grenoble INP, France*; N. Boysen, A. Devi,* Ruhr Universität Bochum, Germany

ALD is a versatile and emerging technology, allowing for the precise coating of challenging substrates with a nanometer control over thickness. Due to its unique assets, a substantial growth of the ALD market is expected. In the current context of moving towards greener processes, the ALD technique offers the potential to become greener and to tackle environmental challenges. Indeed, the process itself has currently a consequent impact on the environment which should ideally be reduced as the technique is implemented in a wider range of products and applications. Based on a literature overview, our findings show that the duration of the process, the temperature used, and the precursor chemistry are key factors affecting the environmental impact of ALD. The principles of green chemistry are discussed considering the specificities of the ALD process, and different ways to reduce the impact are proposed, in particular the optimization of the processing parameters, the use of spatial ALD (SALD) and the chemical design of greener precursors are shown as efficient routes to lower the ALD environmental impact and improve its sustainability.

AF-MoP-3 An IR Spectroscopy Study of the Degradation of Surface Bound Azido-Groups in High Vacuum*,* ***Sofie S. T. Vandenbroucke**, M. Nisula, R. Petit,* Ghent University, Belgium*; R. Vos, K. Jans, P. Vereecken,* IMEC, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

'Click chemistry' encompasses a set of powerful chemical reactions that have a high yield, are highly selective and specific, proceed under simple reaction conditions, use readily available starting materials, create stable products and harmless by-products.[Kolb, H.C., et al. (2001) *Ang. Chem. Int.*] The azide-alkyne cycloaddition reaction is considered the cream of the crop of the click reactions. Hence, surface functionalization by azido-moieties is often desired for applications in drug discovery, polymer chemistry, materials engineering and biosensor devices. [Lahann J. (2009) *Click chemistry for biotechnology and materials science*] This can be achieved by depositing self-assembled monolayers using azido-containing organosilanes which typically involves liquid-phase protocols. The use of vapour-phase chemistry might be beneficial regarding integration into a high-throughput production sequence and the deposition of high-quality and reproducible coatings on 3D microstructures. [Vos, R., et al. (2018) *Langmuir*] Because vapour-chemistry typically involves the use of high vacuum equipment, the stability of the azido-groups in high vacuum is of utmost importance.

In this work,[Vandenbroucke S.S.T. (2021) *Langmuir*] the stability of azido-containing self-assembled monolayers is monitored in real-time using in situ reflection FTIR at a temperature of 150 °C and a pressure of 1E-5 mbar for 8 h. The data in Figure 1 displays a clear decrease of the asymmetric azide stretching vibration at 2105 cm^{-1} over time in high vacuum, suggesting the degradation of the azido-groups. The degradation is further investigated at three different temperatures and seven different nitrogen partial pressures using ex situ ATR-FTIR. The degradation is found to increase at higher temperatures and lower nitrogen pressures. This is in accordance with the theory that the degradation reaction involves the decomposition into molecular nitrogen and the formation of a highly reactive nitrene.

Many applications in the semiconductor industry require a perfect control over the surface chemistry down to the nanometre level to yield reproducible results. For the condition with the most degradation only 63% of azides are found to remain at the surface after 8 h in high vacuum. This would imply a significant loss in control over the exact surface chemistry. One should therefore always consider the stability of functional groups such as azides when depositing or post-processing functional coatings in high vacuum.

AF-MoP-4 Nucleation of AlOx on ZrOx and ZrOx on AlOx studied by Low Energy Ion Scattering*,* ***Jan Tröger**,* Tascon GmbH, Germany*; M. Näsi, T. Blomberg,* Picosun Oy, Finland*; R. ter Veen,* Tascon GmbH, Germany

Nucleation is a crucial step in the formation of ALD films. It determines the formation of the first atomic layer of film. Proper nucleation is needed to deposit closed films with a homogeneous thickness. Since the nucleation deals with the formation of the first atomic layer of film, a very surface specific tool is needed to study nucleation: It should be able to distinguish between a closed monolayer and a half-closed double layer.

For common other techniques, such as XRF or XRR, it is not possibly to make this distinction due to a lack of surface specificity. Low Energy Ion Scattering (LEIS), on the other hand, is specific to the very first atomic layer, enabling it to determine the closure of the film (surface fractions of film and substrate), rather than the overall number of atoms per unit area that XRF or XRR provide.

We will demonstrate how LEIS works for the nucleation of AlOx films on ZrOx and the ZrOx films on AlOx. We show the normalized LEIS peak areas for Al and Zr as a function of cycle number for both depositions. The results show that in both cases, the films are almost closed after 20 cycles. In addition, we will present and discuss the following two features: In the deposition of ZrOx on AlOx, the peak area for Zr "overshoots". This indicates that the initial deposition happens with a stoichiometry that Zr-rich compared to ZrO_2 (and has some similarity to that of the Al_2O_3 substrate). In the case of the deposition of AlOx on ZrOx, the peak area for Al "undershoots", indicating that the initial deposition proceeds with an Al-poor stoichiometry compared to that of Al_2O_3 (with some similarity to that of the ZrO_2 substrate).

AF-MoP-5 Characteristics Evaluation of SiO_2 Thin Film Deposited by Organic vs Inorganic Precursor in ALD

***Jihyeok An**, I. Yang, S. Yoon,* DUKSAN Techopia Co., Ltd, Korea (Republic of)*; I. Park,* Hanyang University, Korea

As semiconductor device highly integrated in a chip, it required a more complex structure at unit devices such as transistor, capacitor, and resistor. The thin film coated in structure needs better thickness controllability and uniformity as well as very smooth surface, especially in the complicated 3D-structure. To fulfill the demand, ALD method, which provided excellent step coverage, has been strongly adopted in the fabrications of metal oxides and metal itself. Silicon oxide(SiO_2) has been the most representative material used for the longest time in semiconductor industry in gate, floating gate, and other processes. The film characteristics of SiO_2 strongly depend on the precursor type and process parameters even though it was made with the same ALD method.

In this work, the process and materials characteristics dependency of precursor type, especially organic or inorganic, have been studied in ALD process and film properties. SiO_2 thin films were deposited by plasma enhanced ALD system with respective organic (tetrakis(dimethylamino)silane, tDMAS) and inorganic (hexachlorodisilane, HCDS) precursor. ALD window region was confirmed for both precursors. The growth rate of SiO_2 films fabricated with tDMAS and HCDS were 0.78 and 0.21 Å/cycle at the deposition temperature of 400℃ and 300℃, respectively. The Si : O ratio of SiO_2 film was 1.9 for tDMAS and 2.0 for HCDS. The density of both films was the same as 2.5. The surface of SiO2 film made with tDMAS, 0.1 nm RMS roughness, is smoother than that with HCDS, 0.5 nm. The MOS devices based on both SiO_2 films were manufactured with Si substrate and TiN metal electrode, and their capacitance properties were analyzed. The dielectric constant of both films showed the same value of 3.9.

AF-MoP-6 Microstructure and Electrical Properties of Conductive Nitride Films Grown by Plasma Enhanced Atomic Layer Deposition with Considerable Ion Bombardment

I. Krylov, Tower Semiconductor Ltd., Israel*; **Valentina Korchnoy**, X. Xu, K. Weinfeld, E. Yalon, D. Ritter, M. Eizenberg,* Technion - Israel Institute of Technology, Israel

We investigated electrical properties and structure of conductive nitrides (TiN_x, ZrN_x, TaN_x, HfN_x) deposited by the PEALD process from amide precursors and H_2/Ar plasma. Ion bombardment introduces additional energy to the growing film promoting chemical reactions and film densification. In PEALD process involving H_2/Ar plasma, most of bombardment effects are related to heavier Ar ions which are responsible for obtaining highly crystalline nitride films. Ion energy depends on the pressure inside ALD reactor during plasma half-cycle. Low pressure is favorable for deposition of highly conductive nitrides. The deposited nitrides have different grain size, carbon contamination, and variation of the film density from theoretical value despite same process conditions. Films crystallinity was investigated by the HAADF-STEM (Fig.1). The deposited nitride films differ in film morphology. TiN_x films consist of large columnar grains elongated through the whole film thickness. HfN_x films has columnar-like grains with smaller grain size compared to TiN_x. ZrN_x and TaN_x films consist of small grains. Significant ion bombardment reached in the process results in the growth of (111)-oriented polycrystalline films with low O contamination (Table1). The films are polycrystalline (Fig.2) despite the significant carbon content. Crystallization is stimulated by the ion bombardment effect achieved by the lowing plasma pressure. Carbon contamination correlates with the level of C-content in the precursor molecule.

Electrical resistivity of deposited nitrides is summarized in Fig.3,a. Despite near similar bulk resistivity of TiN, ZrN, and HfN, a significant difference in resistivity was found in the deposited films. Among the investigated films, TiN_x has the highest grain size and lowest resistivity. Density of the deposited nitrides was measured by the XRR. Deviation of the film density from its theoretical values represents the degree of crystallinity at a given film and follows the resistivity trend. Higher deviation indicates the smaller grain size resulting in higher electron scattering at grain boundaries. Film density can serve as a good qualitative parameter predicting the resistivity of transition metal nitride deposited by PEALD. Positive TCR values (metallic) were obtained for TiN_x and ZrN_x films, whereas the deposited TaN_x and HfN_x films have negative TCR values (semiconducting) (Fig.3,b). Negative TCR values are attributed to the presence of nitrogen-rich phases, $MN_x > 1$ in these films. Among the investigated films, TiN_x films have the highest grain size and lowest resistivity. Therefore, TiN_x is proposed as the leading PEALD nitride for conductive applications.

AF-MoP-7 Room-Temperature Atomic Layer Deposition of Iron Oxide and Its Surface Reaction; Explained by *in-Situ* Observation

*K. Yoshida, I. Nagata, K. Saito, M. Miura, K. Kanomata, **Fumihiko Hirose**,* Yamagata University, Japan

Room-temperature (23- 25˚C) atomic layer deposition (RT-ALD) of iron oxide is developed with a precursor of bis(N, N'-diisopropyl-propionamidinate)iron ($(DIPPA)_2Fe$) and plasma excited humidified Ar. Iron oxide such as Fe_2O_3 is examined as a magnetic coating material for pharmaceutical powders in drug delivery. Since the ALD uses saturation of the surface reaction, it is possible to deposit the oxide film on powder surfaces with nanometer precision. We consider that the ALD could be applied to heat-sensitive pharmaceutical drugs, although there were no previous reports on the RT Fe_2O_3 ALD. To find the gas injection conditions in ALD, we investigate the saturation of precursor adsorption and oxidation on the iron oxide surface in this study. The ALD growth is confirmed by quartz crystal microbalance (QCM). We used plasma excited humidified Ar as an oxidizing gas, and $(DIPPA)_2Fe$ as precursors of iron oxide. Any heaters or thermal sources were not installed on the ALD chamber wall. The $(DIPPA)_2Fe$ container and gas delivery pipe were warmed up around 80 °C to promote the precursor evaporation without its condensation. The exposure of Fe precursor in the adsorption step was 2.0×10^5 Langmuir (L). The oxidation time was set at 600 s. The evacuation steps of 300 and 60 s were inserted between the precursor and the plasma excited humidified Ar injections. P-type Si (100) substrates and polyethylene naphthalate (PEN) films were used for the ALD tests. We confirmed the film composition by XPS with a MgKα X-ray source. For the QCM measurement, we used an ALD sensor (#750-717-G2, Inficon) with AT-cut quartz crystals in which the resonance frequency was 6 MHz. The sampling rate was 2 Hz. We examined the iron oxide deposition on Si(100) and PEN. A sample image of the iron oxide coated PEN is shown in figure 1. The sample is colored brown by the interference of iron oxide thin film, but peelings and cracks were invisible. We confirmed Fe 2p narrow scan spectra of the iron oxide on Si(100) and PEN by XPS. Both of the deposited iron oxide Fe 2p peak positions are indicated the film is stoichiometrically close to Fe_2O_3. These suggest the applicability of the present RT-ALD to heat-sensitive materials. To discuss the surface reaction in this process, we picked up a typical mass variation curve, as shown in figure 2. The number of reacted ligands of the precursor adsorption period is estimated as 1 or 2 from a mass variation ratio during one ALD cycle. In the conference, we report the characteristics of deposited iron oxide and discuss the surface reaction of iron oxide RT-ALD.

AF-MoP-8 Simulation of Conformality of ALD Growth Inside Lateral Channels: Comparison between a Diffusion-Reaction Model and a Ballistic Model

*J. Velasco, J. Järvilehto, J. Yim, E. Verkama, **Riikka Puurunen**,* Aalto University, Finland

A number of models have been developed for simulating the conformality of atomic layer deposition processes.[1] Simulation models can be used, for example, for the optimization of process parameters towards improved conformality, and for the extraction of kinetic-related information through fitting the model parameters to experimental data.[2,3]

Three fundamentally different simulation approaches have been described in the literature to simulate the conformality of ALD processes: diffusion-reaction, ballistic, and Monte Carlo models.[1,5,6] In diffusion-reaction models, transport inside a feature is described by a diffusion equation that includes an adsorption loss term.[1,6] Ballistic models describe particle transport in the molecular flow regime and are based on a balance of particles to compute fluxes at different locations inside a feature.[5] In Monte Carlo models, the path of each particle at a time is simulated.[1]

In this work, we compared the conformality of ALD growth inside lateral channels predicted by two fundamentally different models: a diffusion-reaction model (Model A)[6,7] and a ballistic model (Model B).[5,8] The effect of different operating conditions on the conformality of ALD is studied in the free molecular flow regime.

For all the parameters studied, the main trends of the obtained saturation profiles were similar for both models (Fig. 1 of the supp. info). However, penetration depth at half-coverage predicted by the ballistic model was greater than that predicted by the diffusion-reaction model while the predicted slope at half-coverage was greater with the diffusion-reaction model (Fig. 2 of the supp. info). The ballistic model predicted a sudden increment of coverage when the profile reaches the end of the channel. The reasons and consequences of the differences will be discussed.

This work was supported by the Academy of Finland (ALDI consortium, grant No. 331082). An earlier version of this work was presented at the 21st Int. Conf. on Atomic Layer Deposition, ALD 2021.

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AF-MoP-9 Chemisorption of Aminosilane Precursors on OH-terminated SiO_2 Surfaces during ALD of SiO_2*, Heeju Son*, *k. Khumaini, H. Roh, H. Kim, W. Lee,* Sejong University, Korea (Republic of)

Understanding the surface reaction mechanism is required to design and improve the atomic layer deposition (ALD) process. The ALD reaction mechanism can be studied by simulating the chemisorption of silicon precursor by density functional theory (DFT) calculation, which agrees well with the experimentally observed results [1]. The ALD SiO_2 using an aminosilane-type precursor, such as DIPAS ($SiH_3(N^iPr_2)$), BDEAS ($SiH_2(NEt_2)_2$), or TDMAS ($SiH(NMe_2)_3$), is being used in various dielectric deposition and patterning processes. DFT studies simulated the chemisorption of the Si precursor, assuming that dialkylamino ligands combine with H atoms of OH groups to form amine molecules as the byproduct. However, there was no report considering the type and distance of the hydroxyl groups on the surface. Also, comparative studies with experimental results are lacking. Therefore, in this study, we compared the chemisorption of aminosilane-type precursors on various OH-terminated SiO_2 surfaces modeled with different hydroxyl types and distances by DFT simulation. We also compared the chemisorption mechanisms of the precursors having different numbers of dialkylamino ligands. Reaction energies were calculated for all possible reaction pathways, assuming the release of amine or H_2 as the byproduct, and then the activation energies were obtained for exothermic pathways. The surface species predicted by DFT simulation well explains the experimental results from in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared (FTIR) spectroscopy.

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AF-MoP-10 Volatile Adducts of Cobalt and Nickel Halides*, Timo Hatanpää*, *A. Vihervaara, M. Ritala,* University of Helsinki, Finland

Volatile metal halides in general are good ALD precursors as they are simple, cheap, readily available, thermally stable, reactive with many non-metal precursors and small in size allowing good growth rates. Unfortunately, halides of many metals are not volatile or they possess only low volatility. Many of such metal halides can, however, be rendered more volatile by adding proper adduct ligands to the metal coordination sphere.

Earlier we have introduced diamine adducts of cobalt and nickel to ALD. While pure halides of Co and Ni have polymeric solid-state structures, high melting point and low volatility, the diamine adducts have monomeric structure and volatility that is among average for known Co and Ni precursors. Under reduced pressure these compounds sublime intact and have sufficiently large temperature window between the sublimation and decomposition temperatures. These compounds have also been shown to perform well in ALD.[1]

For metal films low deposition temperatures are desired to minimize agglomeration and thereby obtain smoother films that are continuous at lower thickness. High volatility of the metal precursor is therefore needed. Here more adducts of the transition metal halides, especially phosphine adducts, were synthesized and studied.

While diphosphine adducts of Co and Ni are thermally exceptionally stable, their volatility is low. In contrast, monophosphine adducts of the same are highly volatile but the thermal stabilities are low. For example $NiCl_2(PEt_3)_2$ sublimes already at 80 °C under vacuum, but signs of thermal decomposition are also seen already around 130 °C. The temperature window is still large enough to allow ALD usage as demonstrated by Ni metal film deposition using this precursor (another ALD2022 presentation).[2] Monophosphine adducts of Co have lower volatility than the Ni counterparts so that the temperature window between efficient evaporation and thermal decomposition is narrower.

In this presentation the thermal properties of cobalt and nickel halides with different neutral ligands including amines and phosphines are presented and compared. Among other things, it has been found that the thermal stability mainly increases from chlorides to iodides and the trend seems to be more pronounced with cobalt. The increasing molecular weight from chlorides to iodides causes only small decrease in volatility.

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AF-MoP-11 Fabrication of Aluminum Nitride with 160 °C Atomic Layer Deposition using Plasma Excited Ammonia*, Kentaro Saito*, *K. Yoshida, M. Miura, K. Kanomata, B. Ahmmad, S. Kubota, F. Hirose,* Yamagata University, Japan

Aluminum nitride (AlN) has been attracting much attention since it is also expected to be used as a passivation layer for AlGaN/GaN high electron mobility transistors. In the conventional technologies, AlN depositions were examined by atomic layer deposition (ALD), although these were performed at a temperature of 200 °C and higher. To suppress solid-phase diffusion of the passivation layer, a low-temperature deposition is demanded. In this study, the low-temperature ALD of AlN using trimethylaluminum (TMA) and plasma-excited ammonia is examined. We evaluated chemical composition in the AlN films deposited at 160 °C by secondary ion mass spectrometry (SIMS) and cross-sectional transmission electron microscope (cross-sectional TEM), respectively. To confirm its applicability to a gas barrier, we try to deposit AlN on PET.

TMA was used as an Al precursor. Plasma-excited ammonia was used as a nitridation gas. For its generation, 4.2 sccm ammonia and 1.8 sccm argon were mixed, followed by being excited with an RF power of 250 W and a frequency of 13.56 MHz. TMA was introduced with an exposure of 1×10^5 L ($1L=1\times 10^{-6}$ Torr・s). The nitridation time was 180 s.

We observed the interface layer to examine if the film was deposited on the substrate without solid phase diffusion. The chemical composition was evaluated to measure impurity in the AlN film. Fig 1. shows a cross-sectional TEM image obtained from the AlN with the 150 cycles ALD. We see the polycrystalline AlN film on the starting surface without damage to the Si substrate. To propose the application to a gas barrier, we examined to deposit AlN on PET. Fig. 2 shows an image of an AlN deposited PET sample. From Fig.2, it is considered that the AlN deposition on PET is performed without the thermal deformation of the film. The water barrier characteristics are going to be disclosed in the conference for the further discussion.

AF-MoP-12 On the Underestimation of the Low-Temperature Limit for ALD of MoO_x from $Mo(CO)_6$ Precursor*, Kees van der Zouw*, *T. Aarnink, A. Kovalgin,* University of Twente, Netherlands

Dependencies of the growth rate per cycle (GPC) as a function of the temperature (T), and the so-called precursor saturation curves, are standardly observed for atomic layer deposition (ALD) and reflect its self-limiting nature. Such curves are considered as an indication of the ALD window and required to demonstrate the occurrence of ALD at various circumstances. Plotting GPC versus T is expected to be system independent, meaning that the fundamental features of the GPC curve should be similar between one reactor system and another. It looks feasible to underestimate the limits of the ALD window if there is no universal method to determine the GPC. Based on our experimental findings, we propose an underestimation of the ALD temperature window to occur in the literature study on the (self-limiting) chemisorption of $Mo(CO)_6$ while depositing molybdenum oxide (MoO_x) and molybdenum oxide compounds.

According to the literature, the use of $Mo(CO)_6$ as precursor and O_3 or O_2-plasma as co-reactant results in the self-limiting chemisorption of $Mo(CO)_6$ roughly between 150 and 175 ^oC. The GPC is mentioned to quickly decay for temperatures below 150 °C, with hardly any deposition at T<130 °C [1,2]. According to the experimental observations in this work, the deposition of MoO_x on a silicon substrate can indeed hardly start at T<130 °C, due to the practically inappropriate long incubation time. However, the deposition of MoO_x, once enabled at T=130 °C or higher, naturally continues at 80 °C with a reasonable GPC. The growth per cycle decreases only from 0.028 nm/min at T= 175 °C to 0.020 nm/min at T= 80 °C.

In our presentation, an extended look into these experimental findings including film characterization will be given. We further would like to draw attention of the ALD community to a need for verifying the methodology of ALD window determination for scientific experiments.

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AF-MoP-13 $ZnO_{1-x}S_x$ Layer Growth and Composition by Thermal and Plasma ALD*, Stefanie Spiering*, *D. Bagrowski, T. Magorian Friedlmeier, W. Hempel, T. Wohnhaas, J. Becker,* Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Germany

$ZnO_{1-x}S_x$ alloys are wide-bandgap materials with high transmittance in the short-wavelength region. This makes them promising candidates as the n-type conducting buffer layer for different absorber types in thin-film photovoltaic devices. In this work, we studied the growth behaviour and composition of ternary $ZnO_{1-x}S_x$ on Si wafer substrates at a fixed deposition temperature of 150°C using a thermal ALD process with diethylzinc (DEZ), H_2O and H_2S as precursors, and additionally a mixed thermal/plasma-enhanced ALD process with DEZ, H_2S and O_2 plasma. The growth rates and the composition of the films were analysed by spectral ellipsometry and EDX (energy dispersive x-ray spectrometry).

With thermal ALD we processed layers over a wide range of different H_2O:H_2S pulse ratios. The cycle ratio for H_2S is defined here as CR_{H2S}=k*100%/(k+l) with k being the number of H_2S pulses and l being the number of H_2O pulses in a cycle, respectively. In contrast to former works on $ZnO_{1-x}S_x$ by ALD, not only the smallest possible bilayer period P=1*(k+l) for a certain CR_{H2S} was applied, but also larger bilayer periods P=a*(k+l) were examined (e.g. a=1,2,…,7 for CR_{H2S}=50% (k:l = 1:1) à P=2,4, …,14).EDX measurements showed a significant influence of the bilayer period on the sulphur content in the resulting films. Furthermore, we observed a linear relationship between the resulting S/(S+O) ratio in the film and the number of H_2S pulses for a fixed number of H_2O pulses, and vice versa. Therefore, it is possible to estimate the S/(S+O) ratio for a given pulse ratio by extrapolation. We discuss a few exceptions to the linear behaviour, e.g. for H_2O:H_2S ratio 1:1, 1:l and k:1.

$ZnO_{1-x}S_x$ films grown in a mixed thermal-/plasma-enhanced ALD process showed a very different layer growth in comparison to the thermal deposition. With the purely thermal process we deposited layers with S/(S+O) ratios in a wide range from about 10 to 90 % applying moderate $H_2S/(H_2O+H_2S)$ pulse ratios, even a higher S-content in the layers was achieved compared to the theoretically expected one. In contrast, by application of oxygen plasma (O_2Pl) as reactant for the ZnO cycle, a very high H_2S pulse fraction was necessary to reach S/(S+O) ratios >30%. With an O_2Pl:H_2S ratio of 1:24 (CR_{H2S}=96%) a S/(S+O) ratio of 60 % was measured.

AF-MoP-14 Effect of Precursors on Properties of Atomic Layer Deposited Cr-Ti-O Thin Films*, Mahtab Salari Mehr,* University of Tartu, Institute of Physics, Estonia*; L. Aarik,* University of Tartu, Istitute of Physics, Estonia*; T. Jõgiaas, A. Tarre, H. Mändar,* University of Tartu, Institute of Physics, Estonia

Abstract:

Chromium oxide coatings are technologically important due to their good mechanical, chemical, magnetic, catalytic and optical properties. It has been shown that the properties of Cr_2O_3 coatings can be considerably changed if it is doped with an appropriate element. Chromium containing ternary oxide thin films have previously been grown by chemical vapor deposition or magnetron sputtering methods resulting in hard (hardness 31 GPa) [1]orsuper-hard (40 GPa) coatings [2] or showing good photocatalytic properties [3]. In this work chromium containing ternary compound (Cr-Ti-O) thin films were grown on Si (100) substrates using two different precursor combinations: CrO_2Cl_2 -CH_3OH:$TiCl_4$-H_2O, and $Cr(thd)_3$-O_3:$TiCl_4$-$O_3$by atomic layer deposition offering precise control over the concentration of dopant elements in the composition. Film density, roughness, phase composition, refractive index, hardness and Young's modulus were studied in variation of Ti concentration in the thin films. Thin films with average thickness of 115 nm deposited using CrO_2Cl_2-CH_3OH and $TiCl_4$-H_2Oprecursors exhibited crystalline α-Cr_2O_3 (eskolaite) phase with density from 4.8 to 5.2 g/cm^3. By increasing the number of $TiCl_4$ -H_2O cycles compared to CrO_2Cl_2-CH_3OH cycles, the total intensity of eskolaite reflections decreased. The films with average thickness of 45 nm deposited using $Cr(thd)_3$-O_3 and $TiCl_4$-O_3showed crystalline TiO_2 anatase phases with density from 4.0 to 4.7 g/cm^3 (Fig. 1). As the growth rate of the Cr_2O_3 deposited using $Cr(thd)_3$-O_3 (50 pm/cycle) was remarkable lower than that for CrO_2Cl_2-CH_3OH process (70 pm/cycle), the change of the $Cr(thd)_3$-O_3:$TiCl_4$-O_3 cycle ratio from 1:30 to 1:1 only decreased the amount of the anatase phase in the film.

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AF-MoP-15 Ligand Exchange with a Novel Cyclic Alkyl Amido Plumbylene and Transition Metal Complexes*, Kieran Lawford,* *G. Bačić,* Carleton University, Canada*; J. Masuda,* St. Mary's University, Canada*; S. Barry,* Carleton University, Canada

Lead-containing precursors are an active field of study for the deposition of PbS (DOI: 10.1021/acs.chemmater.0c01887), PbO (DOI: 10.1149/1.2789286), and other lead-containing films.During our efforts to find new Pb(II) ALD precursors, we found that the acyclic diamido plumbylene lead(II) bis(*N-tert*-butyltrimethylsilylamide) (**0**) undergoes facile thermal decomposition into the homoleptic cyclic (alkyl)(amido) plumbylene (caaPb) bis(*N-tert*-butyl-2-aza-3,3-dimethyl-1-plumba-3-silacyclobutane) (**1**). Our interest in compound **1** pivoted toward the novel nature of the ligand and the potential to use it to synthesize new ALD precursors. We hypothesised that salt-metathesis between **1** and metal chlorides would produce similar heterocycles (caaM, M=metal). Lead is a good candidate for salt metathesis due to the thermodynamic driving force of the formation and precipitation of $PbCl_2$, driving the reaction to completion. Additionally, the high yield of the caaPb, cheap starting materials, and recyclability of the $PbCl_2$ by-product makes this synthetic methodology appealing, economical, and green. We tested the metathesis with $ZnCl_2$ because, if the salt metathesis is possible with zinc, then less electropositive metals should also undergo in the ligand exchange. During our test, we isolated $PbCl_2$ indicating that the metathesis was successful. Quantum chemical studies suggests the analogous reaction with other metal chlorides should also proceed.

There are early examples of titanium, zirconium, and hafnium complexes with a similar heterocyclic system ($CH_2Si(Me_2)NSiMe_3$), and the heterocyclic $Cp_2TiCH_2Si(Me_2)NSiMe_3$. was even used as a titanium-ceramic CVD precursor.[1,2] However, the synthesis of these is unreliable.[2] We can now prepare similar metal complexes using ligand exchange from **1** with higher yields. Additionally, we expect to see a change in thermal properties after exchanging the trimethylsilyl group for a t-butyl group appended to the heterocycle, since the trimethylsilyl moiety is thermally active. A variety of complexes will be vetted to determine which work best as vapour-phase precursors with respect to volatility and thermal stability.

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AF-MoP-16 Diaminosilane Precursors for the Atomic Layer Deposition of Iron Metal*, Molly Alderman,* *S. Barry,* Carleton University, Canada

Currently there are few processes for the atomic layer deposition of iron metal thin films, and none without significant limitations—either by CVD or relying on very specific substrates with growth terminating after the initial substrate is covered. With an appropriate precursor, iron films could provide the basis for ferromagnetic coatings and to enable a range of iron alloy films – like stainless steel thin films – with desirable properties.

Geminal diaminosilane (gDAS) ligands are N,N′ κ^2 chelates with silicon bridging the coordinating nitrogen centres (Figure 1). We have previously reported a range of first row transition metal complexes with the gem-diaminosilane (^{t}BuNH)$SiMe_2NMe_2$ [2]. Transition metal gDAS precursors possess better volatility and thermal stability than their amidinate analogues while still avoiding problematic metal-oxygen bonds (compared to alkoxides) and with added stability from the chelate effect.

Here we report our initial study of new iron complexes which improve on the previously reported acetamidinate and α-imino alkoxide precursors [1]. We have synthesized, characterized, and evaluated the thermal characteristics of several Fe(II) and Fe(III) complexes containing monoanionic and dianionic gDAS ligands which show promise as precursors for the ALD of iron. Preliminary deposition studies using the previously reported $Fe(gDAS)_2$ monitored by quartz-crystal microbalance, as well as microscopy and initial compositional analysis will also be discussed.

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AF-MoP-17 Low-temperature Epitaxy of β-Ga_2O_3 Films via Hollow-cathode Plasma-assisted ALD*, Saidjafarzoda Ilhom*, *A. Mohammad, D. Shukla, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*; N. Biyikli,* University of Connecticut

Gallium oxide (Ga_2O_3) is an emerging ultrawide-bandgap (UWBG) semiconductor attracting significant interest for high-power and high-frequency electronics that features comparable electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm) to wide-bandgap GaN and SiC. However, growing device-level high-quality (Ga_2O_3) films have been mainly possible at high substrate temperatures (700 – 1000 °C) using complex reactor settings, which substantially increases the production cost and limits the application space.

In this work, we report on low-temperature as-grown crystalline β-Ga_2O_3 films on Si, glass, and sapphire via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperatures and 50 W rf-power level. Additionally, eachunit ALD-cycle was followed by an in-situ Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. The samples exhibited enhanced growth-per-cycle (GPC) values around 1.3 Å. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 film signature with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the Ga_2O_3 layers grown on sapphire substrates. X-ray photoelectron spectroscopy (XPS) measurements shed light on the elemental composition and provide additional understanding on the nature of chemical bonding states within β-Ga_2O_3 layers. Our results demonstrate the effectiveness of in situ Ar-plasma annealing process within a customized HCPA-ALD reactor setting to transform amorphous wide bandgap oxide semiconductors into epitaxial films at substantially reduced substrate temperatures.

AF-MoP-18 Higher Effective Dielectric Constant of Hafnium Oxide When Grown with Hydrogen Peroxide Compared to Water Vapor*, Jeffrey Spiegelman,* RASIRC*; H. Kashyap, A. Kummel,* University of California at San Diego

As high-k gate dielectrics continue scaling in the sub 1nm EOT range, the low-k interfacial layer that is pre-formed or formed during the dielectric deposition process is increasingly problematic since it reduces the effective k-value of the dielectric layer(1) . For Hafnium Oxide grown on silicon, the EOT is a combination of the silicon dioxide interface and the quality of the hafnium oxide. Consiglio (1) reported reduced thickness of the silicon dioxide interface layer with hydrogen peroxide gas when compared to ozone. In this study hafnium oxide was grown on HF cleaned silicon with either water vapor or H2O2 gas. The Keffective was improved by 27% H2O2 grown HfO2. The film grew 50% faster with H2O2 than water. Vt was 0.18V for H2O2 and -1.3V for water. Additional data will be presented to clarify if the Keffective was due to a thinner SiO2 interface layer or improved HfO2 film quality.

AF-MoP-19 Atomic Layer Deposition of Low-resistivity Molybdenum Nitride Using F-free Mo Precursors and NH_3 Plasma*, Wangu Kang,* *J. Ahn, J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

Molybdenum nitride film (MoN_x) is considered as a promising material in CMOS manufacturing process as gate electrode, contact layer, and diffusion barrier due to its high electrical conductivity, chemical stability, and thermal stability. With the continuous miniaturization of semiconductor devices, the development of atomic layer deposition (ALD) MoN_x process has been demanded to obtain conformal MoN_x film in complex 3-dimensional structure. However, MoN_x ALD using fluorine(F)-containing Mo precursor such as MoF_6showed various issues for example, forming void due to HF fume and degradation of metal or peripheral oxide by HF by-product.
In this study, we have developed the ALD MoN_x films using F-free Mo precursor and NH_3 plasma at the temperature range of 200-400 ^{o}C. The characteristics of MoN_x thin films such as crystallinity, chemical binding state, impurity and resistivity were examined by GAXRD, XPS, and 4-point measurement system. The post-annealing by rapid thermal annealing (RTA) at 500-800^{o}C was conducted in H_2/Ar ambient to improve the resistivity of MoN_x films, and consequently the significant decrease in resistivity was observed after RTA due to the reduction of MoN_x into Mo.

AF-MoP-20 Atomic Layer Deposition of Molybdenum Carbides for Advanced Metallization: The Influences of Mo Precursor and Post-Deposition Annealing*, Ji Sang Ahn,* *W. Kang, J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

As the width of metallization wire in semiconductor device decreases, Cu interconnect and W word line does not scale down as fast as linewidth due to its high electron mean free path (EMFP). Meanwhile, molybdenum (Mo) and molybdenum carbides (MoC_x) are considered as promising materials for next-generation interconnect owing to its small EMFP andless resistivity size effect.In order to apply the Mo and MoC_xthin films to the 3-dimensional semiconductor devices, atomic layer deposition (ALD) of Mo and MoC_x has been required. However, Mo and MoC_x ALD using fluorine (F)-containing Mo precursor resulted in various issues such as oxide damage and deterioration of device property due to F contamination and HF by-product. Therefore, it is essential to developMo and MoC_x ALD processusing F-free Mo precursors.

In this study, δ-MoC and β-Mo_2C thin films were depositedby ALD using two different F-free precursors. Rapid thermal annealing (RTA) process was adopted to reduce MoC_x into Mo metal and to increase crystallinity of the film. β-Mo_2C showedimproved crystallinity after RTA process, whereas δ-MoC was reduced into metallic Mo (~46.5 μΩ·cm) after post-reduction annealing. The crystallinity, chemical state, impurity, and electrical characteristics of molybdenum carbide thin films will be compared before and after annealing process and reaction mechanism of the post-reduction annealing will be discussed.

AF-MoP-21 ALD of Niobium Oxide (Nb_2O_5) and Niobium-Doped Titanium Oxide (Nb:TiO_2) for Solar Cell Applications*, Thomas Vincent,* *D. Coutancier, P. Dally,* IPVF (Institut Photovoltaïque d'Île-de-France), France*; M. Bouttemy, M. Frégnaux,* ILV (Institut Lavoisier de Versailles) - IPVF (Institut Photovoltaïque d'Île-de-France), France*; N. Schneider,* CNRS-IPVF, France

Atomic Layer Deposition (ALD) is increasingly contributing to the energy field and more specifically to the engineering of solar cells. Its conformity enables deposition on nanostructured substrates and its low growth temperature allows the deposition on temperature-sensitive substrates such as perovskite.

Niobium oxide, Nb_2O_5, is a wide bandgap semiconductor that has been grown by different methods and has recently been used in solar cells. Its optical and electrical properties depend strongly of the technique used for its growth, opening access to a wide range of application, such as electron transport layer (ETL)or passivation layer [1,2]. It is also used for the doping of titanium oxide (TiO_2), a well-known ETL, to reach a better stability of the complete solar cell.

In this work, we first developed ALD-Nb_2O_5 from tris(diethylamido)(tert-butylimido)niobium (TBTDENb) and water. The growth was studied from 100°C to 200°C, on several substrates (Si, glass, FTO, ITO). The ALD process was first optimized using QCM (Quartz Crystal Microbalance). Annealing studies in different conditions (air/inert atmospheres, up to 600°C) were conducted to understand the evolution of Nb_2O_5 at temperatures which are relevant within the fabrication steps of the solar cell.

Then, niobium-doped titanium oxide was developed using tris(isopropoxide)titanium (TTIP) as titanium precursor, and Nb-doping was applied by a supercycle strategy and tuned by several methods (supercycle ratio, precursors sequences). For both materials, structural, chemical, electrical and optical properties were characterized by XRR (X-Ray Reflectivity), GIXRD (Grazing Incidence X-Ray Diffraction), ellipsometry, SEM (Scanning Electron Microscopy), XPS (X-Ray Photoelectron Spectrometry), XRF (X-Ray Fluorescence), spectrophotometry, 4-points probe.

Finally, those ALD-materials were implemented in perovskite solar cell architectures.

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AF-MoP-22 Understanding the Grown Mechanism of Al_2O_3 Thin Films Using Plasma-Activated Deionized Water as Oxygen Source on Thermal ALD*, **William Chiappim**,* Aeronautical Institute of Technology, Brazil*; J. Chaves,* Aeronautical Institute of Technology , Brazil*; B. Botan Neto, L. Gonçalves de Lima, M. Shiotani Marcondes, N. Galvão, A. da Silva Sobrinho, R. Sávio Pessoa,* Aeronautical Institute of Technology, Brazil

The atomic layer deposition (ALD) of metallic oxides, mainly alumina (Al2O3), when performed in thermal mode, uses deionized water (DI) as an oxygen source and trimethylaluminum (TMA) as a metal reactant. However, growth per cycle (GPC) of Al2O3 thin films for the reactant and co-reactant mentioned above is limited to 0.1 nm/cycle. This barrier in the GPC is overcome by using plasma technology as an oxygen source. This technique is commonly called energy-enhanced ALD because the plasma oxygen source provides tremendous activation energy during the co-reactant step, which allows for greater efficiency in generating active sites on the substrate surface, promoting thus more reactions between the surface and the metal reactant. This process, called plasma-enhanced ALD (PEALD), is commonly used to replace DI water with O2 plasma as an oxygen source [2]. It is reported in the literature that for the TMA reactant, this replacement of the vapor phase oxygen source (thermal ALD) by a plasma oxygen source (PEALD) generates an increase in the alumina GPC to 0.12 nm/cycle, i.e., a gain of 20%. However, this gain in the GPC has a high cost, as the PEALD uses a source to generate the plasma that uses electrical energy to ionize and dissociate the gas introduced into the chamber. In addition, it is necessary to design a new deposition chamber and design the entire electrical system to turn it into equipment that operates in plasma mode, which significantly increases production costs. The present work presents a cheap alternative to increase the GPC of alumina by 20%. A gliding arc plasma and compressed air were used to activate DI water. Plasma-activated water (PAW) was prepared by a forward vortex flow reactor (FVFR) type with air compressed at atmospheric pressure. The activation times were 10, 30, and 60 min, and it was reached the following pH of 3.5, 3.0, and 2.5. PAWs were characterized by UV-vis spectrophotometer and presented reactive oxygen and nitrogen species (RONS), namely, H2O2, HNO2, NO2-, and NO3-.

After activation, plasma-activated water (PAW) is carried out into a recipient and introduced in the line of oxygen source in thermal ALD. The ALD pulse times were 0.15-30-0.3-30 s, TMA, N2 purge, PAW, and another N2 purge. The number of cycles was fixed at 1000 cycles, and the substrate was the Si (100). Alumina thin films growth was characterized *in-situ* by mass spectrometry and *ex-situ* by an optical profilometer, FT-IR and FEG-SEM.

According to the characterizations mentioned above, the existing RONS in PAW probably contributed to the activation of sites in the Si(100) substrate, thus increasing the GPC of the alumina.

AF-MoP-23 Atomic Layer Deposition of Titanium Phosphate onto Reinforcing Fibers Using Titanium Chloride, Water, and Tris-(Trimethylsilyl)-Phosphate as Precursor*, **Pauline Dill**, X. Ren, H. Hintersatz,* University of Technology Chemnitz, Germany*; M. Franz,* Fraunhofer Institute of Electronic Nano Systems ENAS, Germany*; D. Dentel, C. Tegenkamp, S. Ebert,* University of Technology Chemnitz, Germany

Thermal ALD process for depositing titanium phosphate on carbon fiber bundles and flat silicon substrates using the novel precursor system titanium tetrachloride, water, and tris-(trimethylsilyl)-phosphate was studied. We observe a linear growth per cycle of 0.22 nm/cycle. Compositional analysis of the coating was investigated using energy-dispersive X-ray spectroscopy (EDXS), and X-ray photoelectron spectroscopy (XPS). The thermal behavior up to 900 °C and the changes compositional were investigated via infrared spectroscopy (IR). With oxidation of coated carbon fibers in the thermogravimetric analysis (TGA) we could show that the coating also increases the onset temperature of oxidation of the fibers.

The coated fibers will be embedded in a ceramic matrix to give a fiber reinforced ceramic matrix composite (CMC). In this CMC the coating has the role induce the deflection of cracks that run through the matrix and to provide oxidation resistance.

P. Dill, X. Ren, H. Hintersatz, M. Franz, D. Dentel, C. Tegenkamp, S. Ebert, *J.Vac. Sci. Technol. A* 40 (**2022**); doi: 10.1116/6.0001514

AF-MoP-24 Amorphous Carbon(a-C) Atomic Layer Deposition using CBr_4 Precursor*, **Tae Hyun Kim**, M. Kim, S. Park, S. Chung, H. Kim,* Yonsei University, Korea

Phase change memory (PCM) is attracting attention as the need for high-performance memory semiconductors that can process large amounts of data quickly increases with the development of the 4th industry, such as big data and artificial intelligence. At the same time, research on 3dimensions cross-point (3D X-point) memory using memory cells and selectors in the area where word lines and bit lines intersect in 3D to create a highly integrated PCM is also being conducted. However, the most important factor for high efficiency and integration of these PCM devices is to reduce the current required for device operation. Recently, studies have been actively conducted to increase the joule heating efficiency by increasing the specific resistance of the electrode. In this respect, carbon, which exhibits various resistivities (conductor (graphite, sp^2 bond) – insulator (diamond, sp^3 bond)) [1], [2] depending on the state of atomic bonding, is an attractive material as a PCM electrode. So far, PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition) processes have been used to deposit carbon thin films. However, it is difficult to deposit a uniform carbon thin film on a three-dimensional structure with the conventional method, and it is difficult to control the physical properties of carbon. Therefore, in this study, a carbon process using ALD (Atomic Layer Deposition) was developed. Furthermore, the analysis of the carbon thin film properties according to the process conditions (reactant, temperature, pressure, time, etc...) was analyzed, and the corresponding mechanism was studied.

AF-MoP-25 Al_2O_3 Nanowire Growth on WSe_2 Flake by Using Low-temperature ALD*, **Chi-Chung Kei**, C. Su, B. Liu,* Taiwan Instrument Technology Institute, National Applied Research Laboratories, Taiwan*; Y. Su,* Department of Electrophysics, National Yang Ming Chiao Tung University, Taiwan*; T. Lee, C. Cheng, H. Wang, I. Radu,* Corporate Research, TSMC, Taiwan*; W. Chang,* Department of Electrophysics, National Yang Ming Chiao Tung University, Taiwan

Transition metal dichalcogenide (TMD) has been considered a promising material for the channel material of electronics due to remarkable electrical characteristics.Atomic layer deposition (ALD) is a promising method to deposit film for TMD-based device fabrication. However, lack of dangling bond on TMDs leads to a chemically inert surface for the chemisorption of ALD precursors.Physisorption of ALD precursors is considered to form seeding or reactive sites on chemically inert surface of TMDs. In this work, WSe_2 flakes were used as the substrate to grow Al_2O_3 by using ALD. 90^{o}C was chosen as the working temperature to allow the physisorption of ALD precursors on WSe_2 substrates. Atomic force microscopic image (AFM) in **Fig. 1(a)** shows the triangular WSe_2 flakes were grown on mis-cut sapphire substrates after meta-organic vapor deposition. WSe_2 surface, shown in **Figs. 1(b)** and **(c)**, exhibits terrace morphologies and is similar to mis-cut sapphire substrate. Terrace width and step-height are estimated to about 80 nm and 0.3 nm, respectively. In the Al_2O_3 ALD, trimethyl aluminum (TMA) and water were used as the sources of aluminum and oxygen, respectively. One ALD cycle for growing Al_2O_3 started with 0.1 s TMA pulse, followed by 18 s N_2 purge to remove excess precursor and by- products, then 0.1 s water pulse, and finally another 18 s N_2 purge. After 20 cycles of Al_2O_3 ALD, nanowire-like structure was formed on the surface of WSe_2 flake, as shown in **Fig. 2(a)**. According to the line-scan data in **Figs. 2(b)** and **(c)**, the width and height of nanowires are estimated to be about 40 and 6 nm, respectively. The peak-to-peak spacing between nanowires, about 80nm, is consistent with the terrace width of WSe_2 surface. This suggests that Al_2O_3 preferentially nucleates and grows along the valley of terrace structure. This can be attributed that the energy barrier to form a stable physisorbed embryos on a concave valley is lower than that on a flat surface. The growth per cycle (GPC) of about 0.3 nm/cycle also suggests that Al_2O_3 growth was both contributed from the physisorption and chemisorption of ALD precursors.

**AF-MoP-26 Comparison of Atomic Layer Deposited ZrO2 Thin Film using Cp-based Zr Precursor and Newly Synthesized Cp-based Zr Precursor*, Hyemi Han,* *S. Park, S. Na, S. Chung, H. Kim,* Yonsei University, Korea (Republic of)

As the dynamic random access memory (DRAM) has been continuous downscaling, zirconium oxide, a high-k dielectric material, is widely used as a substitute for conventional SiO2. Because it has a relative high dielectric constant (15~22), a high breakdown field (15–20 MV/cm), a large band gap (5–7 eV), and a good thermodynamic stability up to 800 ℃ when in contact with the silicon substrate.[1]

Among the various methods of deposition, ALD has been recognized as the leading candidate to process the high-k dielectrics owing to characteristics such as self-limiting reaction, excellent conformality, easy controlled thickness, and large area uniformity.[2]

The choice of precursor is very important because the film properties are totally different depending on which kinds of precursor is used. For instance, in case of halide ligand precursor, it has been widely used since there is no carbon incorporation into the films. However there is limitation like low volatility, particle issue and harmful byproduct. Also alkoxide ligand having a strong metal-oxygen bonding is required a relatively high temperature and it is easily decomposed by heat and contains high concentration of carbon impurity in the thin film. [3] Among various types of precursors, ZrO2 thin film using Cp ligand precursor have been widely used recently due to their good thermally stable allowing deposition temperature above 300℃ and excellent crystallinity. However it has disadvantage in that the growth rate is decreased due to its bulky size.[4]

Like this, several kinds of precursors have been studied for ALD of ZrO2 thin film but it is still needed for research on precursors. In this paper, new linked-Cp zirconium precursor ((linked CpZr(N(CH3)2)3)) was synthesized for ALD of ZrO2 thin film and compared with the commonly used (CpZr(N(CH3)2)3) precursor in terms of growth characteristic and film property. For ALD ZrO2 process, oxygen plasma was used as the oxidant.

Various experimental methods, including spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray Reflectivity (XRR) and density functional theory calculations (DFT)) were used for analyzing growth characteristic and film property. Additionally for the analysis electrical property, capacitance-voltage (C-V) and current-voltage (I-V) measurements were conducted.

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AF-MoP-27 Thermal Atomic Layer Deposition of in_2O_3 Thin Films Using a Homoleptic Indium Triazenide Precursor and Water*, Pamburayi Mpofu,* Linköping University, Sweden

Indium oxide (In_2O_3) has received much attention for a wide range of applications, including in optoelectronics as a transparent conducting material. We report ALD of In2O3 using a recently reported indium(III) triazenideprecursor[1] together with water. The deposition process was studied between 150 and 520 °C using a homebuilt crossflow ALD reactor at 50 hPa with indium(III) triazenide pulsed for 4s, and water pulsed for 3s as precursors and purging with nitrogen for 10s in between. The deposition process is self-limiting at ~1.0 Å/cycle and temperature window between 270 and 385 °C. XRD analysis shows that the films are polycrystalline with a preferred (222) orientation. The films are substoichiometric with have low levels of C impurities. Optical transmittance is high, >70% in visible light, and the resistivity was found to be low signifying high conductivity. These results are on par with the current state-of-the-art reported for thermal ALD of In_2O_3 from a formamidinate precursor.[2] We make a direct comparison between the indium triazenide precursor and the indium formamidinate precursor in the same reactor and show that they render very similar temperature windows and film quality optical transparency, and conductivity of the deposited films.

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AF-MoP-28 Nanoindentation of Amorphous Aluminium and Tantalum Oxide Nanolaminates*, Helle-Mai Piirsoo,* *T. Jõgiaas, P. Ritslaid, K. Kukli, A. Tamm,* University of Tartu, Institute of Physics, Estonia

Ta_2O_5-Al_2O_3 nanolaminates are potentially applicable as high dielectric strength insulators [1], resistive switching media [2] and corrosion resistant coatings [3]. For most applications the mechanical properties of the thin films have a significance on the reliability of the devices. Double- and triple-layer amorphous Al_2O_3-Ta_2O_5 laminates with an overall thickness of about 70 nm were atomic layer deposited while changing the sequence of the layers from surface to substrate. Hardness and elastic modulus of the laminates were measured with nanoindentation and influence from the layer thickness and sequence on the mechanical properties were analysed.

Figure 1 depicts the change of hardness along the depth of the films for double-layered laminates. Layered structure caused an uneven rise in hardness with depth dependent on the sequence of Al_2O_3 and Ta_2O_5. Figure 2 describes the hardness of triple-layered laminates, showing an even incline for the laminate with a middle Ta_2O_5 layer surrounded with Al_2O_3 whereas the laminate with middle Al_2O_3 between Ta_2O_5 layers resembled the double-layered laminate behaviour. An additional quadruple-layered laminate was measured and showed a steady increase of hardness with depth. The elastic modulus for all the laminates was similar, steady along the depth and fell between 145 – 155 GPa.

It can be concluded that the hardness of layered films is affected by both the thickness of the layers and their sequence. Lowering a single constituent layer thickness can smoothen the difference in hardness along the film depth which could reduce internal stresses, defects, and delamination. Adding an extra layer to a thin film could increase its mechanical resilience in a cost-effective way.

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AF-MoP-29 Experimental and ReaxFF MD Studies for Boron Nitride ALD Growth from BCl_3 and NH_3 Precursors*, Naoya Uene,* *T. Mabuchi,* Tohoku University, Japan*; M. Zaitsu,* Japan Advanced Chemicals Ltd., Japan*; Y. Jin,* Japan Advanced Chemicals Ltd., Japan, China*; S. Yasuhara,* Japan Advanced Chemicals Ltd., Japan*; A. van Duin,* Pennsylvania State University, USA*; T. Tokumasu,* Tohoku University, Japan

Boron nitride (BN) has been considered a promising dielectric material for 2D material-based electronics. The atomic layer deposition (ALD) technique is a good method to grow conformal and ultrathin materials at relatively low temperatures. However, the growth mechanism is still not clear because the surface events with self-termination resulting from chemical reactions and physical dynamics are complicated. We aim to understand the growth mechanisms of the BN-ALD process from BCl_3 and NH_3 by experiments and simulations using the reactive force-field molecular dynamics (ReaxFF MD).

First, we investigated temperature profiles using a thermal ALD system described in Fig. (a). BN films were grown on the Si(100) surface in a hot walled horizontal reactor through the general ALD cycles as follows; BCl_3 exposure, Ar purge, NH_3 exposure, and Ar purge. Fig. (b) shows the thickness of the grown BN as a function of growth temperature measured on thechamber wall. We obtained a relatively small dependency of growth per cycle on the temperature in the range of 700-900 °C, suggesting ALD growth. The thin film property was characterized using IR spectroscopy as shown in Fig. (c). The remarkable peak at 1367 cm^{-1} is originated from sp^2 BN associated with the in-plane stretching.These experimental results mean proper BN growth on the Si(100) surface by ALD. Second, we started to develop a new force field for the ReaxFF MD, which can simulate the surface events including complicated chemical reactions and physical dynamics. The initial force field is based on the two types of force field; boron nitride nanostructure formation and dynamical crack propagation in silicon, by Lele et al. and Buehler et al., respectively. The initial force field is mainly trained for boron chloride species and the reaction of BCl_3 on the

OH-terminated Si(100) surface. We simulated one ALD cycle after thermal annealing to relax the initial system shown in Fig. (d). The Ar purge steps are simply replaced as the removals of gas molecules with thermal annealing. The simulations revealed some growth mechanisms: the -BCl_2 chemisorbed on the OH-terminated surface in the feed step, -NH_2 chemisorbed on the Cl-terminated surface in the reaction step, and HCl was generated with the chemisorption in these two steps. Our simulations are still one ALD cycle, however, these growth mechanisms are chemically straightforward.

We will show you thin film properties such as crystallinity and composition and compare them with the experimental results. The experimental and theoretical study of the ALD can be applied not only to the BN system but also to critical materials such as TiN and GaN in the future.

AF-MoP-30 Enhancement of Graphene-Related and Substrate-Related Raman Modes Through Dielectric Layer Deposition*, **Karolina Pietak**,* Warsaw University of Technology Faculty of Chemistry, Poland*; J. Jagiełło, A. Dobrowolski,* University of Warsaw Faculty of Physics, Poland*; R. Budzich,* Warsaw University of Technology Faculty of Chemistry, Poland*; A. Wysmołek,* University of Warsaw Faculty of Physics, Poland*; T. Ciuk,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

Enhancement of the Raman signal intensity is currently among the most researched directions in developing Raman-based characterization techniques of all 2D materials as it elevates detection limits of their fine structural properties. The interest in signal intensification is also triggered by the wide range of applications it can benefit, including biochemistry and biosensing, polymer and materials science, catalysis, electrochemistry, the study of high-temperature processes, and detection of hazardous gases.

In this research, we demonstrate a method for the enhancement of Raman active modes in hydrogen-intercalated quasi-free-standing epitaxial Chemical Vapor Deposition graphene and the underlying semi-insulating 6H-SiC(0001) substrate through constructive signal interference within the atomic-layer-deposited amorphous Al_2O_3 passivation. We find that an optimum Al_2O_3 thickness of 85 nm for the graphene 2D mode and 82 nm for the SiC longitudinal optical A_1 mode at 964 cm^{-1} enables a 60% increase in their spectra intensities. We demonstrate the method's efficiency in Raman-based determination of the dielectric thickness and high-resolution topographic imaging of graphene surface [1].

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Acknowledgements:

The research leading to these results has received funding from the Research Foundation Flanders (FWO) under Grant No. EOS 30467715, the National Science Centre under Grant Agreement No. OPUS 2019/33/B/ST3/02677 for project "*Influence of the silicon carbide and the dielectric passivation defect structure on high-temperature electrical properties of epitaxial graphene*" and the National Centre for Research and Development under Grant Agreement No. LIDER 0168/L-8/2016 for the project "*Graphene on silicon carbide devices for magnetic field detection in extreme temperature conditions*".

Karolina Piętak and Rafał Budzich acknowledge financial support from the IDUB project (Scholarship Plus programme).

AF-MoP-31 Interface Modification of Thermoelectric Materials with Oxide Compounds by Atomic Layer Deposition*, **Shiyang He**, A. Bahrami, K. Nielsch,* Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e.V., Germany

In thermoelectric materials, phase boundaries are crucial for carrier/phonon transport. Manipulation of carrier and phonon scatterings by introducing continuous interface modification has been shown to improve thermoelectric performance. In this work, a strategy of interface modification based on powder atomic layer deposition (PALD) is introduced to accurately control and modify the phase boundary of pure bismuth. Ultrathin layers of Al_2O_3, TiO_2, ZnO and Sb_2O_x are deposited on Bi powder by typically 1–20 cycles. All of the oxide layers significantly alter the microstructure and suppressed grain growth. These hierarchical interface modifications aid in the formation of an energy barrier by the oxide layer, resulting in a substantial increase in the Seebeck coefficient that is superior to that of most pure polycrystalline metals. Conversely, taking advantage of the strong electron and phonon scattering, an exceptionally large decrease in thermal conductivity is obtained. It's worth noting that a substantial decrease of κ_{tot} from 7.8 to 5.7 $W\cdot m^{-1}\cdot K^{-1}$ was obtained with just 5 cycles of Sb_2O_x layers and a 16% reduction of κ_{lat}. Finally, a maximum figure of merit, *zT*, of 0.15 at 393 K and an average *zT* of 0.14 at 300–453 K were achieved after 5 cycles of Al_2O_3-coated Bi. The ALD-based approach, as a practical interfacial modification technique, can be easily applied to other thermoelectric materials to enhance their performance.

AF-MoP-32 Comparative Study of the Growth Characteristics and Electrical Properties for Atomic Layer Deposited HfO_2 Films Using Cp-Based Hf Precursors*, **Seunggyu Na**, S. Park, H. Yoon,* Yonsei University, Korea*; Y. Lee,* Stanford University*; S. Chung, H. Kim,* Yonsei University, Korea

Scaling down of Si-based metal-oxide-semiconductor (MOS) has been main issue for semiconductor industry. With the demand for faster and smaller devices, channel length and thickness of gate dielectric have rapidly shortened. To prevent high leakage current for thin SiO_2, scaling down requires materials with higher dielectric constant. Among many materials, HfO_2 has been widely used for its superior properties. It has appropriate band offset with Si (~1.4 eV) and superb dielectric properties, such as high dielectric constant of about 25. For deposition of gate dielectric HfO_2, atomic layer deposition (ALD) technique has been widely used due to its superior characteristics, including excellent conformality, easily controlled thickness at atomic scale, atomic level composition control, large area uniformity, low impurity, and low growth temperature.

Many kinds of precursors, such as halides, alkoxides, alkylamides, and cyclopentadienyls have been studied for HfO_2 ALD process. Among these various type of precursors, alkylamide precursors are attracting attention due to their superior characteristics. They have relatively weak metal-N bonds, and weaker bond attributes to high reactivity in low temperature. Furthermore, the ligands of alkylamide precursors effectively prevent neighboring precursors from bonding to the metal center, which attributes to low melting point and high volatility. However, their weak metal-N bonds lead to decomposition of the precursors at high temperature. It limits ALD window and results in incorporation of impurities in film at high process temperature. In addition, the upper process temperature limit also prevents the formation of films with higher density and higher crystallinity.

To overcome this low thermal stability issue, heteroleptic precursors including cyclopentadienyl (Cp) ligand were introduced. Cp ligand has been widely employed for enhancing thermal stability and volatility of precursor. To take step further in terms of stability, we studied precursor with linking between Cp ligand and alkylamide ligand. By comparing the two Cp-based heteroleptic precursors with the linking between Cp ligand and alkylamide ligand and the one without, we investigated the impact of linked ligand structure on growth characteristics, chemical compositions, crystallinity, and electrical properties. Furthermore, density functional theory (DFT) calculations were introduced for revealing the reaction energy and pathways.

AF-MoP-33 Role of Ligand Coordination Sphere on the Physico-Chemical Properties of New Mn Precursors: Structural, Thermal and DFT Investigations*, **Martin Wilken**,* Ruhr-Universität Bochum, Germany*; A. Muriqi, M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; A. Devi,* Ruhr Universität Bochum, Germany

The interesting redox chemistry of manganese (Mn), its high abundancy in Earth's crust and additionally the associated unique electronic states make manganese-based materials like its oxides, nitrides or the sulfides suitable for a broad range of applications. In particular, when applied as thin films, Mn-based materials can function as cathodes or components in batteries[1], electrocatalysts for oxygen evolution reaction (OER)[2], dilute magnetic semiconductors (DMS) in spintronics[3] etc. Atomic layer deposition (ALD) is one of the preferred methods to deposit thin films with a high degree of control of film properties. The precursors employed for ALD play an important role. Many of the known Mn precursors namely manganocene's (e.g., $[MnCp_2]$)[4], carbonyls $[Mn_2(CO)_{10}]$[5], or β-diketones (e.g., $[Mn(thd)_3]$)[6] are associated with insufficient vapor pressure, poor shelf life and/or low thermal stability. One particular precursor which potentially overcomes the mentioned drawbacks is the all-nitrogen coordinated manganese tert-butyl-acetamidinate $[Mn(^tBuAMD)_2]$[7]. Motivated by this promising development, we further explored this class of Mn precursors by introducing the structurally related guanidinates and formamidinate ligand systems. This resulted in a series of new Mn complexes, which were thoroughly investigated by means of single-crystal XRD, nuclear magnetic resonance spectroscopy (NMR-Evans method), elemental analysis (EA), mass spectrometry (MS), and infrared spectroscopy (IR). To gain insights into the physicochemical properties, detailed thermal analysis was performed. Owing to the extreme sensitivity and reactivity of the compounds towards moisture and oxygen, density functional theory (DFT) calculations were performed to evaluate the origin of the pronounced reactivity. Based on the interesting results from the DFT studies, we investigated the influence of the manganese coordination sphere moving from all nitrogen to mixed O/N coordinated complexes, to optimize the physicochemical properties. The resulting Mn-ketoiminate class of compounds were successfully isolated and characterized in detail. A direct comparison of the all N- with the mixed O/N-coordinated Mn precursors in terms of the precursor characteristics relevant for ALD applications was performed which will be presented in this contribution.

AF-MoP-34 Surface Reactions During Nitrogen-Based Plasma Irradiation in Plasma-Enhanced Atomic Layer Deposition (PE-ALD) of Silicon Nitride,

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Plasma-enhanced atomic layer deposition (PE-ALD) plays an important role in uniform thin films deposition for semiconductor manufacturing with a large area and high accuracy. Silicon nitride (SiN) thin films are widely used in semiconductor devices. Typical technical challenges of developing PE-ALD of SiN (and any other materials) are to form the films with desired qualities at relatively low surface temperature, and possibly on specific surfaces exclusively (i.e., area selective ALD). In a typical SiN PE-ALD process, Si and chlorine (Cl) containing precursors such as dichlorosilane (DCS) H_2SiCl_2 are adsorbed on the surface in the first half-cycle, and in the second half-cycle, Cl atoms are removed and SiN is formed by nitrogen(N_2) / hydrogen(H_2) or NH_3 plasmas. In the first half-cycle, the adsorption of precursors ends after a monolayer of Si is formed on the SiN surface with bonds terminated with Cl atoms, therefore the half-cycle is self-limiting. In the subsequent half-cycle, the plasma-based process is supposed to replace Cl on the surface with N and H atoms. The goal of this study is to understand the effects of nitrogen ions and hydrogen radicals on the removal of Cl atoms from the surface. We used molecular dynamics (MD) simulations to analyze how the Cl-terminated surface interacts with incident N_2^+ ions and H radicals. The simulation results showed that most Cl atoms are removed with H radical irradiation with and without N_2^+ ions after H dose around $1.3x10^{16}$ (H atoms/cm^2). Incident N_2^+ ions also remove Cl atoms from the surface while they nitride Si deposited on the surface, but the amount of Cl removed from the surface is limited in this case. In addition, knock-on collisions transfer some Cl atoms to a deeper layer, enhancing the Cl contamination of the surface. Incident NH_3^+ ions also remove more Cl atoms than N_2^+ ions only. This means that H plays an important role in converting desorbed precursors such as DCS to SiN in the N_2/H_2 or NH_3 plasma irradiation step. It was also confirmed that MD simulation results and available experimental observations showed good agreement.

AF-MoP-35 Effects of Oxidant and Substrate on Film Properties and Interlayer Formation of Atomic Layer Deposited ZrO_2 Films,

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In the early stage of dynamic random access memory (DRAM) development, the thickness of the dielectric SiO_2 has been reduced in the Si based two dimensional structure to obtain high integration density and capacitance. However, as the DRAM devices have been continuously scaled down, thickness of SiO_2 reached a fatal limit of reaching the physical thickness at which leakage current due to tunneling effect occurs. To break through this, SiO_2 was replaced by high dielectric constant (k) materials[1]. Among the various high-k materials, ZrO_2 is one of the promising materials since it has good thermal stability, high dielectric constant (k~30) and wide bandgap (5.16-7.8 eV)[2,3]. However, when high-k thin film is deposited on TiN, which is widely used as an electrode, the electrical properties of the thin film are deteriorated such as increased leakage current density due to the interlayer formed between high-k film and TiN[4,5].

The interlayer formed between the substrate and dielectric film occurs due to the oxidation of the electrode during the film deposition process, which is affected by the potential barrier height of the oxidation reaction[6]. Since the potential barrier height depends on the work function of the metal electrode, proper selection of the electrode is required. Studies have been reported on replacing the top electrode with Pt, Au, Ag, etc.[6], but these have the disadvantages of being expensive, which makes difficult to easily apply to real industry. Recently, Ru is recognized as a promising material because of its good thermal stability, low resistance, high work function, and relatively inexpensive among noble metals[7]. In this study, we used sputtered Ru as a top electrode and compared effects of bottom electrode using Ru and TiN on ZrO_2 film properties. In addition, to find the proper oxidant to reduce the oxidation of the substrate, the film properties using the two oxidants (oxygen plasma and hydroperoxide) were also compared and analyzed. For ultrathin high quality ZrO_2 film, atomic layer deposition (ALD) has been used, which can secure atomic layer controlled ZrO_2 film with high conformality and high uniformity.

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AF-MoP-36 Zinc Precursor Development for Future ALD Film Applications,

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ZnO has attractive physical properties such as being an intrinsically n-type semiconductor, having a wide bandgap and high electron mobility. Recently, we have seen an increasing number of stable p-type ZnO devices. Furthermore, 2T0C (two transistor zero capacitor) configuration using IGZO (indium gallium zinc oxide) transistor has been deemed a strong candidate for future 3D memory devices thanks to extremely low I_{off} of IGZO TFTs [1]. Diethyl zinc (DEZ) is the preeminent zinc precursor used to make many types of Zn-based ALD thin films such as zinc oxide, sulfide and nitride [2]. However, DEZ has poor thermal stability and can leave carbon impurities in zinc-based films grown at elevated temperatures. Furthermore, it has been pointed out that DEZ has an undesirable pyrophoric nature when exposed to air. Over the years, we have synthesized many kinds of zinc precursors (amide, alkyl, alkoxide, β-diketiminato, β-diketonato, etc.) which have a wide range of TGA delivery temperatures (Fig.1) and thermal stabilities in order to be compatible with future ALD applications. One interesting example of a new ALD Zn precursor is $[Et_2NCH_2CH_2CH_2]_2Zn$ named as ZNP-2 whose structure has two zinc-carbon bonds with pendant amines at the ligand terminal. Fig.2 shows the cross-sectional SEM image of the ALD ZnO film which was made using the ZNP-2 precursor and H_2O as the co-reactant at 200℃. In addition to the ZNP-2 precursor, we will introduce more detailed structures and physical properties on the other zinc precursors as well as some ALD film data during the conference.

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AF-MoP-37 Conformal Deposition of B_xC Thin Films from Triethylboron,

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Boron carbide (B_xC) films enriched in ^{10}B is a promising neutron converter material for the next generation solid-state neutron detectors. Upon neutron irradiation, ^{10}B produce detectable particles by the nuclear reactions $^{10}B + n^0 \rightarrow {}^7Li$ (0.84 MeV) + ^4He (1.47 MeV) + Υ (0.48 MeV) and $^{10}B + n^0 \rightarrow {}^7Li$ (1.02 MeV) + ^4He (1.78 MeV) that have 94% and 6% probability, respectively. Since the world has a ^3He shortage, ^{10}B solid-state detectors can potentially be a replacement to ^3He detectors in large scale neutron facilities. For the next generation high resolution ^{10}B detectors, films enriched in the ^{10}B isotope must be deposited on pixelated sensor-chip substrates with high aspect-ratio morphologies. For such geometries, the currently employed magnetron sputtering technology is limited which highlight the need for alternative deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). In addition, a low temperature process is required since the detector requires ohmic contacts which needs to be coated before converter layer deposition.

For coating high aspect-ratios, ALD would be the obvious choice, but the lack of ALD carbon precursors as well as carbide processes makes conformal continuous CVD processes a promising synthesis route. From our investigation, we report moderate temperature CVD of B_xC thin films on silicon substrates with 8:1 aspect-ratio morphologies, using triethylboron (TEB, $^{nat}B(C_2H_5)_3$) as single source CVD precursor. Step coverage (SC) calculated from the cross-sectional scanning electron microscopy measurements shows that films deposited at ≤450 °C were perfectly conformal (SC = 1). We attribute this to the low reaction probability at low substrate temperatures enabling more gas phase diffusion into the features. The quantitative analysis using time of flight elastic recoil detection analysis (ToF-ERDA) and X-ray photoelectron spectroscopy (XPS) reveals that the as deposited films at 450 °C deposition temperature are B rich carbide material i.e., around 80% Boron, 15% carbon and 5% impurities, which is a promising B/C ratio for neutron detector application if ^{10}B isotope enriched TEB is used. The density of the material, measured by X-ray reflectometry measurements, varies from 1.9 to 2.28 g/cm^3 for the deposition temperatures varying from 425 to 550 ºC in steps of 25 °C.

This study shows that B_xC can be grown conformally by CVD at temperatures matching the thermal budget for the fabrication process and with a total B content which is on par with current state-of-the-art $^{10}B_4C$ films from neutron converters deposited by magnetron sputtering.

AF-MoP-38 Effect of Insulator-to-Metal Transition (Imt) in Vo₂ Deposited by ALD

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Since its discovery in 1959, vanadium dioxide (VO_2) is well-known for its Insulator-to-Metal Transition (IMT) around 70 °C just above room temperature (RT). Over the last decade, it has gained interest because of its potential applications for resistive switching systems, energy storage in lithium-ion batteries, supercapacitors, infrared detectors, or thermochromic materials[1]. Due to its low-temperature process, Atomic Layer Deposition (ALD) offers a real industrial advantage in the growth of VO_2, allowing to run deposition with low energy consumption and therefore low cost, and on substrates that can be temperature sensitive.

In this context, vanadium oxide films were deposited on both silicon (100) and glass substrates at 240 °C from vanadium tri-isopropoxide (VTIP) and water as an oxidizing agent. Films were grown with different thicknesses, ranging from 30 nm to 120 nm, and then annealed for one hour under forming gas (95% Ar, 5% H_2) at a temperature ranging from 400 °C to 550 °C by 50 °C steps.

According to a structural analysis held by X-ray diffraction (XRD) and transmission electron microscopy (TEM) as-deposited vanadium oxide films were amorphous and change morphology to polycrystalline with an admixture of VO_2 and V_2O_5 phases having crystallites size reaching 300 nm after annealing. The elemental analysis was performed by RBS and XPS studies will also be presented for a deeper understanding of their composition and stoichiometry.

VO_2 films were also characterized electrically and optically using resistivity measurements, and spectroscopic techniques such as Raman, FTIR, ellipsometry. All experimental results show a reversible and reproducible IMT around 70 °C for films annealed at 500 °C. For electrical measurements, the resistivity decreases down to 10^{-1} Ω.cm upon IMT temperature. The optical ones show a particularly interesting result by FTIR spectroscopy on VO_2 films on silicon substrate, with an optical absorbance of 0.1 OD at RT which increases up to 0.9 OD above IMT temperature on a wavenumber range extending from 4000 to 1000 cm^{-1}. The phase transition is also observable in the UV-visible range on VO_2 films on glass substrate and is correlated with the appearance or disappearance of low-temperature VO_2 peaks in Raman spectroscopy.

In conclusion, vanadium oxide films deposited by ALD were analyzed between RT and 100 °C and present promising properties tunable with temperature, especially in the IR range, and paves the way for future applications in thermochromic materials.

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AF-MoP-39 New ALD Processes for Y₂O₃ Using Molecularly Engineered Yttrium Formamidinates

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Yttrium oxide (Y_2O_3) thin films have been a subject of intensive research, particularly as an alternative high-k dielectric, due to its high relative permittivity (e_r ~17-20) and large bandgap of 5.5 eV. Furthermore, its high chemical resistivity and mechanical strength facilitate its application as a passivation layer in many fields.

Atomic layer deposition (ALD) has been established as one of the most promising techniques for the growth of high-quality layers for the above mentioned applications. As the precursor selection plays a pivotal role in an ALD process, the development of compounds with an optimal combination of volatility, reactivity and thermal stability is needed.

Besides the established Y precursors, such as β-diketonates or cyclopentadienyls, the all-N coordinated class of the amidinates[1] and guanidinates[2] has emerged as a promising class for the fabrication of yttrium-based materials. Recently, the structurally related formamidinate (famd) ligand class (*N,N'*-dialkyl-formamidinato) was explored, exhibiting a high volatility, reactivity, and stability.[3]

In this study, we focused on the systematic molecular engineering of Y formamidinates to fine–tune the physicochemical properties through a variation of the alkyl side chains. Among the four evaluated precursors, the *tert*butyl-substituted $[Y(^tBu_2\text{–famd})_3]$ showed an increased thermal stability and high reactivity towards H_2O, as revealed by thermal analysis and density functional theory (DFT) studies, respectively.

Subsequently, a thermal ALD process for Y_2O_3 using H_2O as co-reactant was developed, yielding dense *fcc*-Y_2O_3 films on Si substrates with smooth topography. Owing to the appealing structural, compositional and morphological quality of the layers, the process was used to deposit Y_2O_3 as a dielectric component in metal insulator semiconductor (MIS) capacitor structures.[4] The promising electric properties set a strong platform for in-depth studies to understand the interplay between precursor chemistry, ALD process development and integration in capacitor structures.

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AF-MoP-40 Nb/V-Doped Transparent Conductive TiO₂ Films Synthesized by ALD: Effect of Dopant Content and Growing Conditions

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Titanium dioxide (TiO_2) is a wide bandgap (3.0-3.20 eV) material that presents high transparency in the visible range; besides, it has a high refractive index. TiO_2 doping is widely investigated to induce structural and electronic modifications that may improve electronic properties and photocatalytic activities. Due to their additional electron compared to Ti and their atomic radius slightly above and below the one of Ti, Nb and V are the most promising candidates among the potential dopants of TiO_2. In this context, this work aims to synthesize Nb/V-doped TiO_2 films by atomic layer deposition (ALD) with various dopant concentrations and growing conditions.

Nb/V-doped TiO_2 films were deposited on Si wafer and glass substrates with water as oxidizing agent using a shared ALD window for precursors niobium (V) ethoxide or vanadium (V) oxytriisopropoxide and titanium isopropoxide, respectively. The dopant content was adjusted by the dopant ratio (*R_{Nb} or R_V*: range from 0 to 1), which is the number of dopant cycles over the total number of ALD cycles. Films were then annealed in N_2 or forming gas (95% N_2 and 5% H_2) at different temperatures of 400, 500, and 600 °C for 1 hour. To investigate the characteristics of films, various techniques, such as spectroscopic ellipsometry, spectrophotometry, GI-XRD, Raman, FTIR, HRTEM, XRR, and four-probe resistivity were used for the as-deposited and annealed Nb/V-doped TiO_2 films.

It was observed that when introducing Nb or V into the TiO_2 matrix up to a doping ratio of 0.025, the thickness increased slightly compared to the undoped TiO_2 film, and then gradually decreased as the dopant ratio increases further. For both dopants, the refractive index and the electronic density of films were found to evolve similarly and in the opposite way to their thickness. In the as-deposited Nb-doped TiO_2 films with R_{Nb} = 0-0.025, the presence of the crystalline anatase phase was identified, but the peak intensity decreased and progressively shifted as R_{Nb} increased. In the case of the as-deposited V-doped TiO_2 film, only an amorphous phase was obtained which transform into crystalline phase with annealing.

After annealing, the optical transmittance and electrical resistivity of anatase phase crystallized films were measured for Nb/V-doped TiO_2 films. With increasing R_{Nb}, the films showed transmittance ranging from 60 to 80% in the visible range, which increase with the conductivity (~10^2 S.cm^{-1}). The optical and electrical properties of V-doped TiO_2 film are also performed and will be further discussed.

This work highlights the significant role of Nb and V dopants in tuning the structural, optical, and electrical property of TiO_2.

AF-MoP-42 Atomic Layer Deposition of Tin Oxide Thin Films Using a New Liquid Precursor Bis(methylcyclopentadienyl) Tin*, **Makoto Mizui**, N. Takahashi, F. Mizutani,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M. Inoue, T. Nabatame,* National Institute for Materials Science, Japan

Transparent conductive oxide thin films, including In-Sn-O (ITO), Zn-Sn-O (ZTO), and In-Zn-Sn-O (IZTO) films, have attracted attention for various applications such as flat-panel displays, sensors, and solar cells. We have reported the atomic layer deposition (ALD) of In_2O_3 and ZnO thin films using cyclopentadienyl-based precursors [1, 2]. In order to deposit such transparent conductive oxide thin films by ALD, ALD-Sn precursor is indispensable. This time, we report ALD of tin oxide (SnO_x) thin films using a new liquid cyclopentadienyl-based precursor.

Bis(methylcyclopentadienyl) tin, $Sn(MeCp)_2$, was synthesized as a liquid precursor. Differential scanning calorimetry (DSC) was conducted to measure its thermal decomposition temperature. The decomposition temperature was estimated approximately 220 °C, so the deposition temperature was set to 200 °C, which is the same temperature in the case of ALD of In_2O_3 and ZnO thin films [1, 2]. The vapor pressure of $Sn(MeCp)_2$ was determined by directly measuring equilibrium vapor pressures at several points. From the Clausius-Clapeyron plot for $Sn(MeCp)_2$, the precursor temperature was set to 130 °C, which corresponds to the vapor pressure of approximately 10 Torr.

SnO_x thin films were deposited on 150 mm Si wafers with native oxide films. ALD process was conducted by using $Sn(MeCp)_2$ as a precursor, and remote O_2 plasma as an oxidant. Linear growth of SnO_x thin film was observed when 0.1 s $Sn(MeCp)_2$ and 10 s O_2 plasma pulse times were applied. The growth per cycle (GPC) was approximately 0.06 nm/cycle with this ALD condition. This growth rate was rather slow compared with a previous experiment using tetrakis(dimethylamino)tin (TDMASn) as a precursor and remote O_2 plasma as an oxidant (~0.11 nm/cycle) [3]. One possible reason is that the deposition density was small due to steric hindrance of MeCp ligands. On the contrary, by applying H_2O for 10 s in the place of O_2 plasma, GPC was significantly small (~0.005 nm/cycle).

SnO_x thin films were deposited by ALD using a new cyclopentadienyl-based precursor $Sn(MeCp)_2$, and linear growth of SnO_x thin film was confirmed.

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AF-MoP-43 Growth Rate of Atomic Layer Deposition of Zinc Oxide Thin Films Using Bis(*n*-propyltetramethylcyclopentadienyl)zinc*, **Fumikazu Mizutani**, M. Mizui, N. Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M. Inoue, T. Nabatame,* National Institute for Materials Science, Japan

We have reported the atomic layer deposition of zinc oxide thin films using cyclopentadienyl-based precursors, bis(*n*-propyltetramethylcyclopentadienyl)zinc, $Zn(Cp^{pm})_2$, which is expected to deposit high-purity ZnO thin films [1, 2]. At that time, ZnO thin films were deposited at 200 °C on 150 mm Si wafers with native oxide films, and the ALD process consisted of alternating exposure to $Zn(Cp^{pm})_2$ and oxidants, H_2O followed by an O_2 plasma. However, the growth rate (GPC) was very small, about 0.02 nm/cycle or less. Until then, the precursor was supplied by vapor draw type or Ar assist type, so it was presumed that the reason for the small GPC was the low chemisorption coverage for low supply of the precursor. Therefore, we tried to increase the GPC by supplying the precursor by Ar bubbling type, which can supply a sufficient amount of precursor even at a low vapor pressure.

Other than supplying $Zn(Cp^{pm})_2$ by Ar bubbling, ZnO thin films were deposited on 150 mm Si wafers with native oxide films as before, and the ALD process consisted of alternating exposure to $Zn(Cp^{pm})_2$ and oxidants, H_2O followed by an O_2 plasma. As previously reported, the Clausius-Clapeyron equation for $Zn(Cp^{pm})_2$ is $\log_{10}P$ (Pa) = -2502 / T (K) + 8.84, so the temperature of $Zn(Cp^{pm})_2$ was set to 70 °C where the vapor pressure of $Zn(Cp^{pm})_2$ is 0.3 Torr. The ZnO thin film was deposited for 30 cycles with the H_2O pulse time and the O_2 plasma pulse time fixed at 30 s and 15 s, respectively, and increasing the $Zn(Cp^{pm})_2$ pulse time from 5 s to 30 s. The film thickness of the obtained ZnO thin film increased as the pulse time increased, and was saturated around 20 s. The film thickness was about 7 nm when the Zn pulse time was 20 s to 30 s. Therefore, the GPC is about 0.2 nm/cycle or more, which is an extremely large increase compared to the previous GPC of about 0.02 nm/cycle or less.

Next, when a ZnO thin film was deposited with a $Zn(Cp^{pm})_2$ pulse time of 30 s, an H_2O pulse time of 30 s, and no O_2 plasma pulse, it was deposited without nucleation delay, and the film thickness was about 8 nm. Without the O_2 plasma pulse, the GPC would be slightly larger, as OH groups remained on the surface during the $Zn(Cp^{pm})_2$ pulse, increasing the amount of chemisorption.

Thus, if this $Zn(Cp^{pm})_2$ precursor is sufficiently supplied by Ar bubbling or the like, it can be deposited on a silicon wafer with a native oxide film without nucleation delay, and a large GPC of 0.2 nm / cycle or more can be obtained.

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AF-MoP-44 Monte Carlo Simulation in a Laptop for Understanding Physical Interaction of Atomic Layer Deposition Precursors*, **Bonwook Gu**,* Incheon National University, Korea (Republic of)*; N. Le, C. Nguyen,* Incheon National University, Viet Nam*; S. Yasmeen,* Incheon National University, Pakistan*; K. Youngho,* Incheon National University, Korea (Republic of)*; H. Lee,* incheon National University, Korea (Republic of)

Since the reaction of atomic layer deposition (ALD) strongly depends on surface property, understanding of surface reaction mechanism between substrates and precursors is essential to predict and interpret thin film deposition in ALD. Recently, the many researchers have studied chemical reactions of ALD using density functional theory (DFT) and physical reaction using molecular dynamic (MD). However, DFT is suit for calculating a few of molecule adsorption but not simultaneous multiple adsorptions, and MD is not proper for a large scale simulation due to huge computing resource and long calculation time. In addition, although the steric hindrance effect between the molecules is an important physical factor for simulation of ALD, but it was not considered as a main variable for simulation. In this study, by adopting several assumptions and approximations, we developed a simple simulation method to understand physical steric hindrance effects of ALD precursors by using Monte Carlo (MC) without huge computing resources and applied the method to study surface reaction mechanism of ALD and area selective ALD (AS-ALD). We calculated the areal coverage of precursor on a specific surface used in ALD and AS-ALD using the MC simulation with a random adsorption model. The simulation results show high consistency agreement with experiment data. Based on the 2D model developed first, we extended the MC simulation to 3D system, and obtained reliable results in bulky precursor systems. The simulation method developed in this study could be applied to many of ALD precursors and AS-ALD inhibitor systems just by using a laptop computer.

AF-MoP-45 Atomic Layer Deposition of Tin Monosulfide Films Using a Novel Cyclic Amide Divalent Metalorganic Precursor and H_2S

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Tin (II) sulfide has emerged as an alternative light absorber and optoelectronics material, but its utilization is limited by lacking of purity due to various oxidation states of Sn. In this work, a better quality and stoichiometric SnS thin films were prepared by atomic layer deposition (ALD) using a novel metal-organic liquid precursor, N, N′-di (t-butyl)-2-methyl-1,2-propanediamino tin(II) (Sn (dmpa)) and H_2S. The current ALD system showed distinctive ALD features, such as a self-limited growth, well-defined wide range ALD window between 75 to 175°C, and direct dependency on the number of ALD cycles on the film thickness. Interestingly, the proposed ALD-SnS process shows relatively high growth rate (GPC) value of 0.13 nm/cycle with no incubation delay at 125°C. DFT calculations are performed to investigate the surface reactions and self-limiting nature of the Sn precursor. The surface reactions are found to be feasible even at room temperature with either low- or high-coverage of the thiol group. The obtained films were characterized by several characterization techniques and found that the crystalline SnS films could be grown even at room temperature (25°C) to a high temperature of 250°C on a thermally grown SiO_2 substrate. Mix phase of cubic (π) and orthorhombic (o) SnS films are possible at below 100°C, whereas only orthorhombic phase is stable at above 125°C and SEM verified that the SnS films with different structures have different surface morphologies. The as-grown SnS film's purity was analyzed using Rutherford backscattering spectrometry, and X-ray photoelectron spectroscopy analyses, confirmed the deposition of a stoichiometric tin monosulfide (S/Sn=1) phase with negligible impurities. The optoelectronic properties (band-gap, refractive index, and extinction coefficient) of the SnS films were further evaluated via spectroscopic ellipsometry (SE) analysis. The results from the SE analysis supported the observed change from mixed π-SnS and o-SnS to o-SnS with increasing temperature and allowed the determination of the energy bandgap (~1.1 eV) and a relatively broad semi-transparent window (up to 3000 nm). This newly ALD SnS process may have an immersive range of favorable prospects to utilize in temperatures compatible applications.

Acknowledgments:This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2021R1A2C1007601). The authors appreciated the financial support from grant LM2018103 by the Ministry of Education, Youth, and Sports of the Czech Republic. The precursor used in this study was provided by Hansol Chemical Co. Ltd., Korea.

AF-MoP-46 Density Functional Theory Study on the Selective Capping of Cobalt on Copper Interconnect

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As the scaling of Cu interconnect systems continues, electromigration (EM) has emerged as a problem. The EM is mainly due to the movement of Cu atoms through the interface between Cu wire and the dielectric barrier. The selective Co capping on Cu improves the interface, resulting in increased EM lifetime. However, studies on the mechanism of the selective growth of Co on Cu over the inter-metal dielectrics are rare. The chemisorption of $CpCo(CO)_2$ on Cu and SiO_2 substrates was studied by density functional theory (DFT) calculation [1]. However, endothermicity on both substrates cannot explain the experimental reports [2]. Therefore, we studied the mechanism of selective Co growth using $CpCo(CO)_2$ on Cu over SiO_2 by DFT. We attempted to build reliable substrate models and consider all possible reaction pathways. We also investigated the roles of H_2 co-reactant and the silylation treatment of SiO_2. The calculation results show that H_2 plays a critical role on the Cu substrate but acts as a spectator on the SiO_2 substrates. The chemisorption was exothermic on Cu by forming H_2CO or CO, and H_2 lowered the activation energy from +1.09 eV to +0.62 eV. Contrarily, the reaction was endothermic on the –OH terminated SiO_2 releasing CO, which explains the origin of selective growth of Co on Cu. The chemisorption on the $–SiMe_3$ terminated SiO_2 surface showed the activation energy of +1.74 eV, which is higher than +1.35 eV on the –OH terminated SiO_2. Therefore, the silylation treatment can effectively improve the selectivity of $CpCo(CO)_2$ chemisorption on Cu over SiO_2, especially at high temperatures. Our DFT simulation successfully explains the mechanism of experimental observations on CVD Co.

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AF-MoP-47 A New Low Temperature PEALD Process for HfO_2 Thin Films

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With its high permittivity and large band gap of E_g = 5.7 eV, HfO_2 is of significant interest for high-κ dielectric layers and excellent resistance ratios as well as fast switching speeds are reported for HfO_2 based memristor devices. To realize these microelectronic components, the deposition of pinhole-free thin films with an excellent uniformity and conformality is required. Owing to its saturative growth characteristics, atomic layer deposition (ALD) intrinsically fulfills these requirements. Plasma-enhanced ALD (PEALD) furthermore allows thin film depositions at low temperatures, as required for future flexible electronics, and is thus the method of choice. To enable the beneficial features of ALD, the physico-chemical properties of the precursor need to be carefully fine-tuned in order to optimize its thermal stability, volatility as well as reactivity. Looking for Hf precursors that fulfill these prerequisites, we investigated new heteroleptic Hf complexes. Starting from the parental Hf dialkylamide, we introduced a chelating formamidinate ligand that stabilizes and shields the Hf center, thereby increasing the thermal stability of the resulting complexe while retaining adequate reactivity and volatility. The resulting bis-(dialkylamido)-bis-(formamidinato) Hf(IV) precursor was synthesized on a multigram scale, structurally characterized and evaluated by thermogravimetric analysis and subsequently employed as a precursor for the deposition of HfO_2 in a PEALD process. Using an oxygen plasma, the typical ALD characteristics of precursor saturation, linearity and ALD temperature window were demonstrated with constant growth of 0.7 Å per cycle from 125 °C to 200 °C on Si(100) substrates. The resulting HfO_2 films were further characterized by RBS/NRA, XPS and AFM, revealing the formation of pure and smooth HfO_2 layers. Compared to our previous work [1] with a closely related guanidinate precursor, shorter plasma pulses were sufficient to achieve ALD growth, preventing the formation of an interfacial SiO_2 layer, as revealed by transmission electron microscopy (TEM). By coating polyimide (PI) foils at temperatures as low as 150 °C, there is a potential of implementing the presented low-temperature HfO_2 PEALD process into the development of flexible electronic devices in the future.

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AF-MoP-48 Density Functional Theory Study on Atomic Layer Deposition of Silicon Nitride using Chlorosilane-type Precursors

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Silicon nitride thin film is an essential dielectric material in semiconductor devices. Recently, three-dimensional vertical NAND flash memory devices utilized it as a charge trapping and sacrificial layers. There have been a variety of silicon nitride ALD processes, including thermal and plasma-assisted schemes. Thermal ALD, which benefits from excellent step coverage, is typically achieved with chlorosilane-type precursors, such as dichlorosilane (SiH_2Cl_2) and hexachlorodisilane (Si_2Cl_6), using ammonia (NH_3) as the co-reactant. The reaction mechanism of thermal ALD was reported by experimental and computational studies [1,2]. However, most density functional theory (DFT) studies focused on a single reaction pathway for each precursor. For disilane or trisilane-type precursors having Si-Si bonds, the comparison between multiple reaction pathways is necessary, which is crucial to have a good insight into the film growth and resulting properties. Thus, in the present study, the comprehensive reaction mechanism of ALD silicon nitride using Si_2Cl_6 and Si_3Cl_8 was studied by DFT. The chemisorption of the silicon precursors was modeled and simulated on an NH_2/NH-terminated silicon nitride substrate. Multiple possible reaction pathways assuming the dissociation of a Si–Si or Si–Cl bond were considered, along with different initial orientations of the precursor molecule. For Si_2Cl_6, the most exothermic reaction pathway was the cleavage of a Si-Cl bond to form $–NHSi_2Cl_5$ surface group along with a $–NH_3^+Cl^-$ as the byproduct. For Si_3Cl_8, the most exothermic pathway was the cleavage of a Si–Si bond, forming $–NHSiCl_3$ and Si_2Cl_5H byproduct. The activation energies of exothermic pathways will be calculated and compared to determine the most feasible pathway.

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AF-MoP-49 PE-ALD of SiO_2 and Ti-doped SiO_2 in High Aspect Ratio Structures using Low Cost Precursors*, **Véronique Cremers**, G. Rampelberg, A. Werbrouck, J. Dendooven, C. Detavernier,* Ghent University, Belgium

PE-ALD of SiO_2 has been well studied in the past years, and has found a lot of applications as e.g. for advanced lithograpy, dielectric material in microelectronic devices, photovoltaics and optical applications. For these purposes where a high film quality is required in combination with a limited throughput, the use of more expensive precursors is justified. However, in recent years PE-ALD of SiO_2 found its way towards high surface applications as e.g. the encapsulation of OLEDS or deposition of anti-reflective coatings where precursor cost is a much bigger issue.

In this work, the PE-ALD growth characteristics of SiO_2 was investigated using four precursors in a different price setting: Bis(diethylamino)silane (BDEAS), (3-Aminopropyl)triethoxysilane (APTES),Tetraethyl orthosilicate (TEOS) and Hexamethyldisilazane (HMDS) (in order of high to low precursor cost price), in combination with oxygen plasma as a reactant.

Although it was possible to deposit SiO_2 with all four ALD processes, a significant difference in growth rate was observed. The growth rate varied from 1 Å/cycle for BDEAS to 0.2 Å/cycle for the TEOS-based process (Figure 1). Further the conformality of the four processes was investigated using macroscopic lateral structures with an equivalent aspect ratio (EAR) of 22. While BDEAS and APTES showed an excellent conformality, TEOS and HMDS showed a coated EAR of only 1 and 2.5 respectively. Here the coated EAR is defined as the EAR where the deposited film thickness equals 50% of the original film thickness.
In order to enhance the growth rate and conformality of these last two processes, TiO_2 subcycles were added to the TEOS and HMDS- based processes using titanium(IV)isopropoxide (TTIP) as a low-cost precursor. Both $Ti_xSi(1-x)O_2$ films showed a strong improvement in growth rate, from 0.2 to 0.5 Å/cycle for the TEOS-based process and from 3.5 to 6.2 Å/cycle for the HMDS-based process, using a 1 TTIP :9 TEOS/HMDS subcycle ratio. Besides the growth rate, also a strong improvement in conformality was observed as is shown in Figure 2. The coated EAR for the TEOS-based process increased from 2.5 to 17.5 and for the HMDS based process from 1 to 12 (in both cases for a 1:9 (TiO_2:SiO_2 subcycle ratio)). These results could be promising when (no-pure) SiO_2 films are required for high surface area applications where a low precursor cost is relevant.

AF-MoP-50 Importance of XPS Investigations of ALD Grown 2D Materials*, **Jhonatan Rodriguez Pereira**, R. Zazpe, J. Macak,* University of Pardubice, Czechia

The success of graphene opened a door for an extensive research and utilization of semiconducting 2D transition metal dichalcogenides materials (TMDCs) displaying a range of unique properties [1]. Molybdenum disulphide (MoS2), a TMDCs benchmark material, has been widely studied for multiple applications. In parallel, 2D diselenide and ditelluride analogues, i.e. MoSe2 and MoTe2, have also attracted important interest due to their intriguing properties, such as a higher electrical conductivity than that of MoS2 among others [2, 3].

Recently, we have demonstrated the ALD synthesis of both 2D MoSe2 [4-7] and 2D MoTe2 [8] (using an in-house synthesized precursors), as well as their outstanding performances in different applications. XPS turned a key tool to provide detailed chemical composition analysis of as-deposited 2D Mo-based TMDCs on substrates of different nature. Besides, the post-performance XPS characterization was appealing since the applications of the aforementioned 2D materials involved chemical and/or electronic processes on the surface and it enabled to identify potential chemical composition changes and physico-chemical photo-electro stability of the 2D TMDCs.

This presentation will thus focus on the XPS as key tool for assessment of chemical composition of both as-deposited and post-performance 2D Mo-based TMDCs, recent experimental results as well as the description of some inherent drawbacks that XPS must face during the analysis of the 2D materials.

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AF-MoP-51 Atomic Layer Deposition for Modification of Various 1D Nanomaterials*, **Jan Macak**, R. Zazpe, H. Sopha,* University of Pardubice, Czechia*; M. Rihova,* Brno University of Technology, Czechia*; L. Hromadko, S. Thalluri,* University of Pardubice, Czechia

One-dimensional nanomaterials – materials with one dimension outside the nanoscale, further noted as 1D NMs – represent a class of very important nanomaterials with continuously increasing importance. Due to their intrinsic features, unique properties and diversity of functionalities, they count among the most widely studied materials nowadays. While considerable research efforts have been spent to synthesize various 1D NMs (e.g. nanopores, nanotubes or nanofibers), limited efforts have been devoted to surface modification and property tailoring of these materials.

However, it is their surface that comes into direct contact with various media (air, gases, liquids, solids) and influences the reactivity, stability and biocompatibility of these materials. The surface and aspect ratio (defined as their diameter to length ratio) influence the performance of these materials in various applications. Considering these facts, it is more relevant to tailor the surface of these materials and to be able to influence their properties and reactivity at the nanoscale, rather than to deal with tailoring their own bulk material composition.

The focus of this presentation is on the modification of two types of 1D nanomaterials – nanotubes and nanofibers. Numerous techniques can be utilized for this purpose, such as for example wet chemical or physical deposition techniques. However, it is only the Atomic Layer Deposition (ALD) that is capable of really uniform and homogenous coating of these 1D nanomaterials, in particular those of very high-aspect ratio.

The presentation will be mainly focused on modification of TiO_2 nanotube layers and various nanofibers of different aspect ratios via ALD.

Experimental details and some very recent application examples [1-10] and structural characterizations of these modified materials will be discussed.

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AF-MoP-52 Atomic Layer Deposition of Cobalt(II) Fluoride Thin Films*, **Elisa Atosuo**, M. Mäntymäki, K. Mizohata, M. Chundak, M. Leskelä, M. Ritala,* University of Helsinki, Finland

Cobalt(II) fluoride, among some other first-row transition metal fluorides, is an excellent cathode candidate for lithium-ion and sodium-ion batteries. These metal fluorides have high theoretical potentials and high energy densities compared to the current oxide-based cathodes. However, although ALD is recognized in lithium-ion and sodium-ion battery research in general, the number of ALD processes for fluoride-based battery materials has remained small. Particularly, these first-row transition metal fluorides have been lacking ALD processes. In this work, we present the first ALD process for cobalt(II) fluoride.

CoF_2 was deposited using $CoCl_2TMEDA$* and NH_4F as precursors. The films were characterized with XRD, EDS, XPS, ToF-ERDA, SEM, and AFM. The deposition temperature range studied was 180–300 °C, and all the deposition temperatures resulted in tetragonal CoF_2, as measured by XRD. Also XPS and ToF-ERDA confirm the films to consist of CoF_2. The impurity content measured with ToF-ERDA is low. Most importantly, the amounts of Cl and N, which are constituents of the precursors, are low, for example 0.53 and 0.08 at-% for a film deposited at 250 °C. The combination of a chloride-based precursor and NH_4F thus seems to work well in this case. The saturation of the growth per cycle with respect to pulse and purge lengths was confirmed at 250 °C, and the growth per cycle saturates to ~1.1 Å. In addition, the film thickness is linearly dependent on the number of applied cycles. Like many ALD metal fluorides, these films are rough, as seen in SEM and AFM. At a deposition temperature of 250 °C, for example, a ~60 nm film has a roughness of 12.6 nm.

*TMEDA: N,N,N′,N′-Tetramethylethylenediamine

AF-MoP-53 Mechanistic Aspects of the Indium Nitride Growth under Atomic Layer Deposition Conditions: A Multiscale Modelling Study

__Giane Damas__, IFM, Sweden*; K. Rönnby,* Linköping University, IFM, Sweden*; H. Pedersen, L. Ojamäe,* Linköping University, Sweden

The wurtzite form from Indium Nitride has semiconducting behavior that, combined with advantageous electron transport properties, has offered potential applicability of this material in the field of electronics and light-emitting diodes.[1] The InN thin film is preferentially obtained using atomic layer deposition (ALD) techniques, with lower temperatures that are beneficial for the crystal stability and enable the utilization of ammonia precursor at such conditions.[2] In the process, trimethylindium is a well-known In precursor that might undergo partial decomposition in the gas phase,[3] resulting in the CH_3 radical release that is expected to affect the initial steps of the reaction mechanism. In addition, this precursor usually leads to high level of carbon impurities that is inconvenient for large scale production. Therefore, this project aims at fully understanding the mechanistic aspects of the adsorption and reaction-related processes leading to the In-rich layer formation for InN crystal growth by using a multiscale approach that comprises density functional theory (DFT) and Kinetic Monte Carlo (KMC) computational techniques.

The atomic-scale periodic calculations are carried out within the Perdew–Burke–Ernzerhof (PBE) level of theory in VASP[4]. Initially, the thermal effects are neglected to enable a more extensive investigation of the relevant reaction pathways. Such effects are then added to approximate the model to the actual experimental conditions (T= 593 K, 1 bar). The outcome indicates that the initial decomposition steps whether they occur in the gas phase or at the surface both lead to the final product, *i.e.*methylindium (MI) chemisorbed at the *hcp* site and ethane. However, the N- rich layer leads to an activation of this process that is found to facilitate the precursor dissociation at the surface environment, with an activation enthalpy $\Delta^{\ddagger}H$ <20 kJ/mol for TMI/DMI displacement towards other stable adsorption sites. In a second step, the hydrogen atoms are subsequentially removed through the involvement of two additional precursor molecules to produce low-weight hydrocarbons. The results also suggest the origin of the carbon impurities to be the CH_3 radical released during the process that in turn can form a strong chemical bond with the N-rich layer. From this point, all data necessary for the KMC simulation at the mesoscale level are acquired, which shall also be presented.

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AF-MoP-54 Simple Nanoscale Thermal Techniques for the Measurement of ALD Grown Thin Films

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Measuring the thermal resistances associated with ALD / MBE grown films is critical for their design and use in the semiconductor industry, however traditional measurement techniques such as Time or Frequency Domain Thermoreflectance (TDTR and FDTR respectively) come with complications limiting their widespread adoption.

In these traditional thermoreflectance techniques, two laser beams serve to heat the sample (pump), and subsequently monitor changes in reflectivity (probe), which corresponds to changes in temperature. In TDTR, the beams are pulsed, and the temperature decay over time is measured. This requires the use of a precisely aligned and calibrated delay stage to temporally offset the pump and probe pulses, making this technique impractical for many. In FDTR, a pulsed or CW beam can be used, and the phase offset between sinusoidal heating and a sinusoidal temperature response is monitored. Difficulties in eliminating a frequency-dependent systematic phase offset may make robust use of this technique difficult. in a more recently developed technique, Steady State Thermoreflectance (SSTR), the magnitude of the temperature response is monitored with varying pump intensity. This is limited to the measurement of one single parameter at a time however, and is typically only sensitive to the dominant thermal resistance in the system. SSTR also requires the use of a reference sample with an identical transducer in order to correlate a voltage as measured via the probe's photodetector to a known temperature rise.

We combine the principles behind SSTR (where the magnitude of the temperature response is roughly proportional to the net resistance), with that of FDTR (where the frequency-dependent response of the material system depends on all thermal properties). By examining the magnitude of the reflectivity response at multiple frequencies, we may now simultaneously measure multiple thermal parameters, such as thermal conductivity, volumetric heat capacity or thermal boundary conductance. This also enables the tightening of uncertainty of measured parameters. To validate this approach, we measure a variety of thin ALD-grown films (2-100nm) on several substrates (sapphire, silicon, diamond). All samples have an 80nm aluminum transducer deposited on top, and we measure the net thermal resistance across the ALD-grown film, in addition to the thermal conductivity of the substrate itself. We also measure bulk substrates, demonstrating the simultaneous measurement of thermal conductivity and heat capacity. We include robust uncertainty analysis to establish upper and lower bounds of measured values, and validate these results with an in-house TDTR system.

AF-MoP-55 Investigation of Tris(trialkylsilyl)Phosphides in Atomic Layer Deposition

__Jaroslav Charvot__, University of Pardubice, Czechia*; M. Barr, J. Bachmann,* University of Erlangen-Nürnberg, Germany*; F. Bureš,* University of Pardubice, Czechia

Phosphides are interesting materials among wide variety of scientific fields. InP and GaP are the most profound semiconductors with application in photovoltaics or electronics. Several ALD depositions of metal phosphides were already presented. Apart from one reported reaction of $P(NMe_2)_3$ with $GaMe_3$ affording GaP,[1] PH_3 or its alkylated analogue $t\mathrm{BuPH_2}$[2]are usually used as a source of P^{-III} ion. Nevertheless, except high toxicity of PH_3, depositions using this precursor are often accompanied with lower reactivity supplemented by plasma activation[3] or laser irradiation.[4] PH_3 may also decompose during the deposition causing high content of phosphorus resulting in non-linear growth.

Trialkylsilyl ligand were utilized in ALD of As,[5] Sb[6] Se[7,8] and Te[7] several times. Its electropositive nature generates negative charge on the deposited atom ensuring high reactivity, while keeping good volatility and thermal stability. For example, tris(trimethylsilyl)phosphide is a favorite precursor for metal phosphide quantum dots. It is fairly volatile and can be distilled even at laboratory pressure. Interestingly, no ALD deposition using this class of precursor has been reported for so far. Therefore, this work aims to investigate tris(trialkylsilyl)phosphides as a potential ALD precursors. Preparation of these molecules will be discussed along with structure/thermal properties relationships and selected phosphides will be tested for thin film deposition in ALD.

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AF-MoP-56 Plasma Enhanced Atomic Layer Deposition of Nickel Oxide from Nickelocene: Growth Characteristics and Photoelectrochemical Performance*, **Shane O'Donnell**, F. Jose, M. Snelgrove , C. McFeely , R. O'Connor,* Dublin City University, Ireland

Owing to its relatively low cost and suitable band edge positions, n-type silicon has been widely investigated as a promising candidate for photoelectrochemical (PEC) water splitting photoanodes. However, its PEC performance is hampered due to rapid corrosion from the electrolyte solution rendering the silicon photoanode inoperable within a short period of use. NiO thin films deposited via atomic layer deposition (ALD) have been used as protective coatings to lessen this corrosion in an effort to enhance PEC performance through distancing the oxidation reaction from the n-Si photoanode surface and operating as an oxygen evolution reaction catalyst [1].

We investigate growth kinetics of a plasma enhanced ALD process as well as the PEC performance of NiO thin films fabricated using nickelocene with O2 plasma co-reactant. We compare the performance of as-deposited NiO films with those reduced to Ni metal by including short H2 plasma steps during the deposition recipe, followed by a long H2 plasma anneal. Films are investigated in detail using quasi in-situ x-ray photoelectron spectroscopy (XPS), without vacuum break. PEC performance was measured to link the effects of varying film deposition parameters and processes on photocurrent output and film surface chemistry.

Through the investigation of various NiO film thicknesses and post deposition treatments, post deposition H_2 plasma annealing of all films thicknesses showed a reduction in photocurrent output and sample stability due to susceptibility to etching effects of the plasma treatment. From the work performed on supercycle deposition processes it is observed that the deposition of Ni films in continuous growth conditions with a post deposition H_2 plasma anneal results in films exhibiting greater contributions of Ni metal along with elevated carbon composition resulting from residual ligands being incorporated in the film during growth. Films where H2 exposure takes place during the growth process exhibit a lower relative carbon contribution due to the reduction of remnant ligands distributed throughout the film. The presence of Ni metal is also seen to be lower in sequentially grown films when compared to their post deposition annealed counterparts of the same number of ALD cycles

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AF-MoP-57 Computational Investigations of Precursor and Deposition Chemistry in ALD and AS-ALD*, **Ralf Tonner-Zech**,* Leipzig University, Germany

The mechanistic details of many ALD processes are hardly understood. Despite the progress made by seminal work of Elliott and others, the chemical complexity of ALD processes requires the continued investigation of many aspects for the precursors and surface chemistry when the target is a comprehensive understanding by theoretical methods. We will show our recent progress made by applying density functional theory and electronic structure analysis approaches to understand aspects of ALD in more detail. Our aim is thereby always to cover the full periodicity of the growth surface to enable a realistic modelling of the experimental conditions. For selected aspects of the ALD process, gas phase screening approaches are suitable, which has been shown in the past and will be validated for our target systems here. We will also show that these investigations can be extended to area-selective ALD (AS-ALD) processes by small-molecule inhibitors (SMIs) and that theoretical modelling can play a crucial role in precursor and SMI design as well as uncovering the underlying principles.

AF-MoP-58 Epitaxial-like Growth of Ga_2O_3 Films on GaN Substrate by ALD using GaCp and Combinations of H_2O and O_2 Plasma Gas and Annealing Process*, **Toshihide Nabatame**, M. Inoue, S. Soeya, T. Sawada, T. Onaya, A. Ohi,* National Institute for Materials Science, Japan*; M. Takahashi, K. Ito,* Osaka University, Japan*; N. Ikeda,* National Institute for Materials Science, Japan*; K. Tsukagoshi,* National institute for Materials Science, Japan

β-Ga_2O_3 is an attractive semiconductor because β-Ga_2O_3 has a large bandgap of 4.5-4.9 eV and a high breakdown electric field of 8 MV/cm for future power device. Large high-quality single-crystal β-Ga_2O_3 wafers can be generally fabricated by melt growth methods such as the floating zone and Czochralski techniques. Also, Ga_2O_3 films have been deposited on various substrates including Si and Al_2O_3 by sputtering, CVD and ALD methods. In ALD studies, Ga_2O_3 thin films were deposited by using various precursors such as $Ga(acac)_3$, $[(CH_3)_2GaNH_2]_3$, $Ga_2(NMe_2)_6$, $Me_2GaOiPr$ and $Ga(CH_3)_3$. In our previous study, we reported to deposit Ga_2O_3 thin films on Si by ALD using pentamethylcyclopentadienyl gallium (GaCp) and combinations of H_2O and O_2 plasma as oxidant gas [1]. We also found that the Ga_2O_3 thin film had an amorphous structure and negligible small residual carbon. However, there has few report characteristics of ALD-Ga_2O_3 film on GaN.

In this paper, we investigated crystal growth of Ga_2O_3 films on GaN substrates by ALD and post-deposition annealing processes.

Ga_2O_3 films were deposited on 3-inch (0001) c-plane GaN wafer (c-GaN) and (10-10) m-plane GaN with off-cut angles of 5° toward the (0001) (m-GaN) by ALD with GaCp and combinations of H_2O and O_2 plasma gas. ALD was performed at 300 °C and the growth per cycle value was 0.06 nm/cycle. 20-nm-thick Ga_2O_3 films on GaN substrates were annealed at 800 °C in N_2. The structure of as-deposited and annealed Ga_2O_3 films were evaluated using in-plane XRD and XRD pole figure measurement.

The as-deposited Ga_2O_3 film on c- and m- GaN substrates dominantly had an amorphous structure because of negligible small XRD peak. On the other hand, in c-GaN substrate, the annealed Ga_2O_3 film had four sharp peaks. These peaks at 2q = 19.0, 38.4, 59.3 and 82.4° were assigned to (-201), (-402), (-603) and (-804) of β-phase of Ga_2O_3, respectively. From the (-201) pole figure measurement, strong peak was also observed in the center. These indicated that epitaxial-like growth of β-Ga_2O_3 film with (-201) was dominantly formed on 3-inch GaN wafer. The epitaxial-like growth of β-Ga_2O_3 film on m-GaN was also observed.

This work was supported in part by JSPS KAKENHI (Nos. JP20H02189 and JP18J22998).

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AF-MoP-59 The Impact of Oxygen Reactants on ALD InOx films using novel dimethyl[N^1-(tert-butyl)-N^2,N^2-dimethylethane-1,2-diamine]indium precursor*, **Seong-Hwan Ryu**, T. Hong, S. Choi,* Hanyang University, Korea*; J. Seok, J. Park,* Hansol Chemical, Korea (Republic of)*; J. Park,* Hanyang University, Korea

The oxide semiconductor has been attention due to its high mobility, low growth temperature, and low off-current characteristics (~10^{18} μA/μm). In particular, there are several reports about the indium oxide (InOx) based materials such as IGZO, IZO, IGO, and IGTO, because it has low resistivity due to the large overlap between indium 5s orbitals forming the electron conduction path. Meanwhile, in terms of deposition technique of oxide semiconductor, atomic layer deposition (ALD) is attractive due to excellent control of the thickness and composition control during deposition. In this regard, several studies are reported depositing InOx with ALD, however, there are few studies about the growth mechanism such as precursor ligand and reactant. In this study, we deposited InOx using ALD with novel indium precursor and different reactants. The InOx grown with different reactants exhibits different material properties including crystallinity and electrical properties even at the same low growth temperature. For InOx analysis depending on different growth temperatures with the different reactants, we conducted X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), grazing-incidence wide-angle X-ray scattering (GI-WAXS), X-ray reflectometry (XRR) and Hall measurement.

AF-MoP-60 Development of an Innovative Method to Find New Efficient Gallium ALD Precursors*, P. Pavard,* CNRS-IPVF, France*; C. Gosmini,* LCM, École Polytechnique CNRS, France*; D. Lincot,* CNRS-IPVF, France*; V. Albin, V. Lair, A. Ringuede,* Chimie ParisTech, PSL University, CNRS, France*; A. Auffrant,* LCM, École Polytechnique CNRS, France*; **Nathanaelle Schneider**,* CNRS-IPVF, France

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

This communication focuses on the development of new efficient gallium precursors to be used in the ALD of oxygen-free gallium-containing sulfide thin films.[2] A series of gallium complexes with chelating nitrogen based ligands (guanidinate, amidinate and triazenides) were synthesized and characterized (NMR, XRD) thanks to modular procedures.[3,4] To assess the thermal stability of the reagents and shed light on their transport in ALD, thermal analysis (TGA, DSC) were realized under N_2 and vacuum to mimic transport conditions. Finally, reactivity studies in solution of established ALD precursors and synthesized complexes provide an insight of surface reactions which might take place in an ALD chamber.

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AF-MoP-61 Detailed Characterization of Bis(tri-isopropylcyclopentadienyl)strontium(Sr(iPr$_3$Cp)$_2$) for the Understanding of SrTiO$_3$ Atomic Layer Deposition*, Young Jae Park,* Samsung Advanced Institute of Technology, Korea (Republic of)*; J. Park,* Korea Research Institute of Standards and Science, Korea (Republic of)*; J. Han, J. Lim, B. Choi,* Samsung Advanced Institute of Technology, Korea (Republic of)*; S. Kang,* Korea Research Institute of Standards and Science, Korea (Republic of)*; C. Baik,* Samsung Advanced Institute of Technology, Korea (Republic of)

The detailed characterization of Bis(tri-isopropylcyclopentadienyl)strontium(Sr(iPr$_3$Cp)$_2$) precursor was conducted to understand growth mechanism in atomic layer deposition of SrTiO$_3$ thin films. First, the adsorption behavior was studied using an in-situ attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The band of the Sr(iPr$_3$Cp)$_2$ spectrum on the Ge crystal surface was identical to that of the spectrum measured in the gas phase, but peak intensity was different. In addition, the absorption characteristics studies were carried out over the Ge crystal temperature in the range of 40～100°C. Upon increasing the temperature, a reduction of absorption was observed. Second, to investigate the volatility of Sr(iPr$_3$Cp)$_2$, vapor pressure curve was determined using thermogravymetric analysis. This method can reduce both precursor amount and time required for the vapor pressure measurement. Furthermore, molecular simulation was applied to explain the interrelationship between those properties evaluated in this study and molecular structure. Our study to understand the detailed behavior of precursor can be provided as useful information for optimization of ALD process and new precursor design.

AF-MoP-62 New Potential Synthesis Route of Molybdenum Nitride Nanosheets by Nitriding Molybdenum Disulphide Deposited by Atomic Layer Deposition (ALD)*, Julien Patouillard,* SIMAP, Grenoble-INP, CNRS, France

The first syntheses of transition metal nitrides are derived from metallurgical processes and consisted in nitriding a powder of the metal or one of its oxides (Oyama, 1992; Toth, 1971). These nitrides were synthesized under severe conditions (T > 1200 °Cz and had low specific surfaces (Marchand et al., 1996). Subsequently, the development of catalytic applications requiring nitride powders with large specific surfaces made it necessary to use processes with more moderate temperatures (700 °C to 900 °C) (Marchand et al., 1996, 1999). These "softer" synthetic routes have developed and been applied to the formation of nitrides from transition metal sulfides.

Among the transition metal disulfides, molybdenum disulfide (MoS$_2$)is one of the most widely studied materials in recent years to synthesis molybdenum nitride due to its availability (E. R. Braitwaite & J. Haber, 1994). MoS$_2$ has a natural two-dimensional structure with the sandwich-like S-Mo-S layers serving as building blocks, in which the atoms in the layer are bonded with strong covalent bonding, while the layers are packed together with weak interlayer forces (Jariwala et al., 2014; Li & Zhu, 2015). In recent years, the emergence of 2D materials and the increase in the demand of metal nitrides nanosheets due to their remarkable physical and chemical properties such as high electrical conductivities, catalytic properties, energy storage, and conversion efficiency aroused a particular interest (Khazaei et al., 2013; Wang & Ding, 2018; Xiao et al., 2017, 2018; Zhong et al., 2016). Thereby, some research group(Sun et al., 2018),(Cao et al., 2020) have demonstrated the transformation of MoS$_2$ nanosheets exfoliated from bulk material into molybdenum nitride nanosheets with ammonia and urea reactive heat treatments, respectively.

In this work, we proposed a method to transform a well-controlled uniform MoS$_2$ thin film deposited by Atomic Layer Deposition into molybdenum nitride (MoN$_x$) nanosheets via an ammonia reactive heat treatment at 700 °C supported by *in-situ* reflectance measurements and *ex-situ* Raman and X-Ray Photoelectron spectroscopy characterizations.

AF-MoP-63 Phase-Transformation of as-Grown Crystalline VOx Films Using Ar-Plasma Annealing During Low-Temperature Hollow-Cathode Plasma-Assisted ALD Monitored via *in-Situ* Ellipsometry*, Adnan Mohammad,* *S. Ilhom,* University of Connecticut*; A. Okyay,* Stanford University*; B. Willis, N. Biyikli,* University of Connecticut

Vanadium oxide films show phase-change properties at different stoichiometries including the famous metal-insulator transition (MIT) for VO$_2$around 70 °C shifting between monoclinic to tetragonal rutile structure phase with temperature change. Such layers have the potential to be used forlow-power electrical switches. The existing VOx ALD reports demonstrate mainly as-grown amorphous VOx films via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant. These amorphous films are shown to transform in various crystalline phases using post-deposition annealing process at high temperatures (typically higher than 500 °C). However, no significant report is yet found on low-temperature as-grown VO$_2$ films grown by thermal or plasma-ALD.

In this study we had two major goals: (i) To demonstrate as-grown crystalline VOx films using our customized hollow-cathode plasma-ALD reactor at substrate temperatures lower than 200 °C; (ii) to further improve the crystalline quality and transform the phase structure of the deposited VOx film into the desired VO$_2$ stoichiometry. We have grown crystalline VOx thin films at substrate temperatures as low as 200 °C using TEMAV as the vanadium precursor and O$_2$ plasma as the oxygen co-reactant. The resulting as-grown film was crystalline V$_2$O$_5$. The recipe for the plasma-ALD experiments was as the following: 0.1 s of TEMAV pulse with 10 sccm of N$_2$-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O$_2$ plasma for 10 s, plasma power 50- 300 W, followed by another 10 s of Ar purge. To provide enough TEMAV dose into the reactor chamber, the TEMAV precursor cylinder is heated at 110 °C. The resulting films are crystalline V$_2$O$_5$ with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

Having accomplished our first goal, our next step is to incorporate *in situ* Ar-plasma annealing process steps to further improve and transform the crystal structure of V$_2$O$_5$ films. Ar-plasma annealing parameters including Ar-flow rate, plasma annealing duration, and subsequent purge time will be investigated via *in-situ* process monitoring and *ex-situ* materials characterization.If successful, the resulting VO$_2$ films will be characterized for their temperature-dependent electrical properties to validate the MIT behavior, paving the way for prototype switch devices.

AF-MoP-64 ALD Process Monitoring and Optimisation by Self-Plasma OES*, Mantas Drazdys,* Centrer for Physical Sciences and Technology, Lithuania*; D. Astrauskytė,* Center for Physical Sciences and Technology, Lithuania*; R. Drazdys,* Center fro Physcial Sciences and Technology, Lithuania*; M. Audronis,* Nova Fabrica Ltd., Lithuania

This work reports on the application of Self Plasma Optical Emission Spectroscopy (SPOES) to perform Process Gas Analysis (PGA) to monitor and optimize thin film atomic layer deposition (ALD) process, carried out using metalorganic precursors and water vapor or oxygen plasma as oxidizers. Depositions were carried out at 150℃ using N$_2$ or Ar as carrier and purging gas. The ALD cycle consisted of four steps: (a) metalorganic precursor pulse, (b) purge, (c) oxidant pulse, and (d) purge. Purge times varied in the range of 2 – 120 seconds to find the optimal value based on the PGA results. We performed SPOES PGA using Broadband Plasma

Emission Monitoring (2B-PEM) of an inverted magnetron-based plasma reactor attached to the ALD process exhaust. The miniature plasma reactor can operate at pressures 7.5e−7 Torr to 7.5 Torr. The sensor signals derived from SPOES data react instantly to composition changes revealing trace amounts of constituents of the process material. We demonstrate how real-time process diagnostics, pump-down monitoring, process condition recognition and end-point detection, all taking place in parallel, facilitate ALD process yield maximisation and reaction by product residue in thin films prevention. Furthermore, the gas analysis technology demonstrated does not require additional (differential) pumping systems to perform analyses.

AF-MoP-65 Growth of Boron Nitride by Atomic Layer Deposition Using the in-Situ Decomposition of Ammonium Carbamate*, Ana Álvarez-Yenes,* *M. Knez,* CIC nanoGUNE, Spain

Boron nitride (BN) is a binary compound of boron and nitrogen alternatively linked which can exist in various crystalline forms, all of them analogous to the carbon allotropes. In each of its forms, BN presents interesting properties that make it a useful material in different applications, especially remarkable in nanotechnology.

The aim of this work is to develop and characterize a new Atomic Layer Deposition (ALD) process for the growth of boron nitride thin films. So far, this has been achieved by using ammonia as the nitrogen providing precursor in combination with a boron halide at temperatures above 400°C. The interest is to obtain boron nitride thin films at reaction temperatures below 275°C. In this work, ammonium carbamate ($NH_4[H_2NCO_2]$) and boron tribromide (BBr_3) are used as precursors. $NH_4[H_2NCO_2]$ is a solid at room temperature which easily decomposes giving a CO_2/NH_3 mixture that can substitute ammonia, making the laboratory work safer and simpler. This work focuses on the analysis of the dependence of the growth rate of the process on its different parameters, aiming to optimize the deposition and predict the thickness of the grown films.

The thin films deposited using this process have been analyzed by means of X-Ray reflectivity, X-Ray photoelectron spectroscopy and electron energy loss spectroscopy among other techniques to conclude that the material deposited is amorphous boron nitride with a 1:1 stoichiometry.

AF-MoP-66 Modelling Atomic Layer Deposition of Noble Metals*, Sylwia Klejna,* AGH University of Science and Technology, Academic Centre for Materials and Nanotechnolog, Poland

The major challenge in metal ALD is the reduction process to yield the metallic target film from metal source that usually comprise of metal cation surrounded by anionic ligands. Existing strategies involve using reducing agent or, counterintuitively, oxidizing agent as second co-reagent. Using reducer as co-reagent, *e.g.* H_2, can lead to an abbreviated cycle, and reduced rate of deposition, when stable metal hydrides are not available. In process using oxidizing agent, *e.g.* O_2, transient metal oxide surface may be generated and that can greatly facilitate noble metal ALD [1]. In this scenario the reduction of metallic center is a result of precursor decomposition at this catalytic surface. The higher growth rate is thus achieved, because the metallic film forms also in the processes of combustion of ligands by the oxidizing agent, however with the danger of surface poisoning and oxide deposition.

Thus, the second co-reactant role is crucial. It is used to eliminate the surface bound species of the metal pulse and, at saturation, to produce a reactive overlayer – the catalytic oxide surface, which is characteristic for a particular noble metal. We therefore first investigate the thermodynamics to understand the self-limiting surface chemistry of the oxidizing co-reagent. We use density functional theory (DFT) to establish order of reactivity as a function of temperature and pressure of noble metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) to form oxides. Next, we examine the thermodynamics of ALD process that includes the transient generation of noble metal oxide.

Finally, we investigate reaction steps involved in the metal nucleation on the example of Pt ALD from $MeCpPtMe_3$ and O_2. We evaluate whether the nuclei of the catalytic surface can be formed during the O_2 co-reactant pulse, i.e. when oxidizing agent is introduced into the ALD chamber to combust hydrocarbon-based ligands into the volatile by-products (*e.g.* CO_2, H_2O). We discuss the possibility of production of transient surface bound OH groups predicted in previous study [2] and other by-products, *e.g.* CH_4 identified in the experiment [3]. The factors that facilitate nucleation are examined. This will allow to propose appropriate reagents and chemical processes to control and improve efficiency of the atomic layer deposition of noble metals.

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AF-MoP-67 Effect of the N-Source on the Growth and Quality of Pe-ALD Tin Thin Films*, Clémence Badie,* Aix-Marseille University, France*; M. Barr, J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; T. Defforge, G. Gautier,* GREMAN, CNRS, Univ. Tours, France*; L. Santinacci,* Aix-Marseille University, France

The thermal ALD of TiN is a well-documented process. The common precursors combination is $TDMAT/NH_3$, for thermal as well as for plasma-enhanced ALD (PE-ALD). However, PE-ALD offers a larger variety of co-reactant (N-sources): N_2, H_2 and N_2/H_2. Building the ALD window of TiN using the recipes from our manufacturer, the PE-ALD processes exhibit a longer cycle duration associated to a slower GPC regarding to the thermal ALD one. This is unexpected since the plasma should enhance the production of reactive species and then promote the deposition process. The GPC should therefore be higher. The aim of this work is to optimize the PE-ALD recipes using two different N-sources: NH_3 and N_2. In addition to shorten the deposition duration, the effects of those N-sources as well as their dilution in Ar and the plasma power on the final properties of the films are also studied. The influence of those parameters has been monitored by in situ characterizations (ellipsometry and optical emission spectroscopy, SE and OES, respectively) and by ex situ characterizations (morphology, composition, crystalline structure and electric properties).

The recipe parameters are adjusted to limit the recombinations of the reactive species generated between the remote plasma source to the substrate. For instance, a large Ar dilution of both N_2 and NH_3 limits the film growth (lower GPC). A gas ratio of 1:1 for N-source and Ar flow is set to the optimal values. This is correlated with the OES spectra presenting that in diluted condition, the intensity of the Ar pics is predominant compared to the N-sources one. This suggests that high Ar dilution hinders the generation of N-reactive species leading to a reduction of the number of reactive species involved in the deposit growth and then, to lower GPC, mainly for N_2 plasma. The applied power (50 to 300 W) has no significant effect on the GPC with NH_3 plasma while, for N_2-based plasma, the GPC is maximum at the highest power. This is consistent with the expected low reactivity of N_2 (inert without plasma activation) as compared to highly reactive NH_3. Note that using NH_3, a thermal contribution cannot be discarded. Those results indicate that producing less active species facilitate their transport by limiting recombinations.

The films grown from both N-sources have a similar roughness, composition and morphology. However, the conductivity, conformality on high aspect ratio substrates (1:25) and the growth rate are better using NH_3-based plasma. The N_2 plasma process exhibits an acceptable film quality and it should be considered as well since it uses a non-harmful gas.

AF-MoP-68 Silicon Nitride Grown by VHF (162 MHz) Plasma Enhanced Atomic Layer Deposition With Floating Multi-Tile Electrodes Using Di(Isopropylamino)Silane and N_2 Plasma*, You Jin Ji,* *H. Kim, K. Kim, J. Kang, D. Kim,* Sungkyunkwan University (SKKU), Korea (Republic of)*; K. Kim,* Massachusetts Institute of Technology, Korea (Republic of)*; D. Kim,* Sungkyunkwan University (SKKU), Korea (Republic of)*; A. Ellingboe,* Dublin City University, Ireland*; G. Yeom,* Sungkyunkwan University (SKKU), Korea (Republic of)

To satisfy the requirements for applications of silicon nitride (SiN_x) at the highly scaled logic and memory devices, high quality films (i.e., low contamination, low roughness, etc.) with high conformality at low temperatures are demanded. To meet the stringent requirements for SiN_x applications, plasma enhanced atomic layer deposition (PEALD) is being extensively investigated as the deposition technique. However, the minimization of plasma damage and lowering the process temperature still remain as issues for SiN_x PEALD processes. In this work, the properties of PEALD SiN_xfilms deposited at a low process temperatureof100°Cwithdi(isopropylamino)silane(DIPAS)andN_2plasmaexcitedbyveryhighfrequency(VHF,162MHz)capacitivelycoupledplasma (CCP) sources with a floatingmulti-tile type electrode and a conventional diode type electrode are investigated and compared in addition to the plasma characteristicsofbothplasmasources. ThePEALDSiN_xfilmdepositedusing thefloating multi-tile electrodeexhibitedhighergrowthrate(~0.6Å/cycle),morestoichiometricfilm (N/Si~0.98), andhigherconformalityinatrenchcomparedtothosedepositedbytheconventi onal VHF CCP.Inaddition,theimprovedelectricalcharacteristicscouldbeobtainedwiththefloatingmulti-tile electrode.The improved properties are believed to be related to the higher plasma density, higher radical density, and lower ion energy bombarding the substrate observed for the multi-electrode type through the enhanced power coupling efficiency between the pairs of multi-electrodes in the plasma source.

AF-MoP-69 Computational Fluid Dynamics Study of ALD Processes: Benchmarking and Validation

***Gizem Ersavas Isitman**, D. Izbassarov, R. L. Puurunen, V. Vuorinen,* Aalto University, Finland

Computational fluid dynamics study of ALD processes: Benchmarking and Validation

Gizem Ersavas Isitman[1] , Daulet Izbassarov[1] , Riikka L. Puurunen[2] , Ville Vuorinen[1]

1. School of Engineering, Department of Mechanical Engineering, Aalto University

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Atomic layer deposition (ALD) is an advanced gas-phase deposition technique [1]. ALD technology is exceptionally effective for obtaining high-quality and conformal coating on high aspect ratio structures e.g in microelectronics, nano-materials, etc. These applications often require high manufacturing costs. Numerical methods provide a great opportunity to optimize the manufacturing process.

In this research, the purpose is to better understand ALD using computational fluid dynamics (CFD) in a porous medium by investigating how the reactive gas flow interacts with the catalytic surface. The ALD process is modeled using a CFD tool called aldFOAM [2]. The surface reactions are based on the irreversible Langmuir kinetics. The approach is validated against standard benchmark problems for non-reacting and reacting cases. First, the solver is validated against non-reacting flow past a single particle and tube banks (e.g Fig.1). Next, the irreversible Langmuir surface kinetics model in aldFoam solver is validated against reference data [3] for high aspect ratio structures. After the validation, the method is applied to investigate the surface coverage on different 2D and 3D shapes (e.g Fig.2) under a range of parameters such as pressure and Reynolds number (Re). It is found that the time to fully cover the surface decreases with increasing partial pressure and Re.

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AF-MoP-70 Feature-Scale Conformality of Atomic Layer Deposition from Continuum to Free Molecular Flow: How Knudsen Number Influences Thickness Profile Characteristics

*J. Velasco, **Christine Gonsalves**, G. Ersavas Isitman, J. Yim, E. Verkama, D. Izbassarov, V. Vuorinen, R. Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) is often chosen over other techniques for thin film growth or surface modification because of its conformality, which originates from the self-terminating nature of the reactions used [1]. It is of paramount importance to understand how the conformality in high-aspect-ratio (HAR) surface features evolves with time and depends on process parameters and chemistry. Many simulation frameworks are available to model ALD growth in HAR features [2,4]: diffusion–reaction models, Monte Carlo models and ballistic models. Most simulation frameworks work in the free molecular flow conditions, where kinetic information of the reactions can be extracted from an experimental thickness profile by a simple slope method [3,4].

As seen in Figure 1, the thickness profile characteristics such as the half-thickness penetration depth $x_{50\%}$ and the slope at this half-thickness penetration depth, strongly depend on the Knudsen number in other diffusion conditions than free molecular flow. While $x_{50\%}$ can be taken as a simplistic measure for “conformality”, the slope carries information of reaction kinetics, specifically of the sticking coefficient. To make interpretations on kinetics from experimental thickness profiles, understanding the flow conditions is of central importance. Specifically, assuming Knudsen flow when it is in reality not valid, would lead to incorrect (too high) interpretation of the sticking coefficient.

Recently [4], we showed that the way the process parameters affect the simulated thickness profile in HAR structures, depends on the diffusion regime: free molecular flow (Knudsen number Kn >> 1) has partly different trends than transition flow (Kn ~1). In this work, we extend the simulations to continuum conditions (Kn << 1). In addition to the previously used 1d diffusion–reaction model [4,5], in this work we also use computational fluid dynamics (CFD) calculations to investigate the processes in 3d.

This work was supported by the Academy of Finland (ALDI project).

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AF-MoP-71 Nucleation Studies of Copper ALD on SiO_2 and Si_3N_4

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Nucleation of ALD metal layers shows several key problems, among others, are nucleation delay and island growth, which prohibit the formation of thin compact metal films. To shed more light on the process of nucleation, we have performed a comprehensive electron microscopy study of the early growth stages of copper films prepared by means of the ALD protocol reported by the group of Karppinen [1] optimized for a hot-wall reactor.

$Cu(dmap)_2$ and HQ were used to grow copper by varying the growth temperature in the range of 120-160°C. Films were grown on Si substrates of different orientations covered with native oxide, on Si/SiO_2 substrates with different thicknesses of oxide layer, and Si_3N_4 membranes. We have observed island growth irrespective of substrate type for a few hundreds of ALD cycles. Moreover, the growth mechanism is influenced by other factors such as the temperature of the substrate as well as the precursor flux. We will report on the coverage density, distribution of island size and chemical composition differs depending on growth conditions. We have resolved mixed compositions varying from metallic copper to copper oxide based on TEM studies. Both, Cu(I) and Cu(II) oxides are present in all the films studied. It is uncertain whether the oxide phase was deposited, or it is formed upon exposure to air during samples transfer from ALD reactor to TEM experimental chamber.

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AF-MoP-72 Photocatalytic Degradation of Harmful Pollutants to Improve Indoor and Outdoor Air Quality

***Tobias Graumann**, S. Pleger, C. Jacobs, C. Beyen, V. Sittinger,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

The application of photocatalytic materials in air treatment and air-borne pollutant remediation has been well established. Photocatalytically active materials used in urban areas on a commercial base can include paints, tiles, and concretes which mainly utilize TiO_2 as the photocatalyst material. Feasibility studies demonstrated the potential of those materials for the use of mineralizing organic compounds into carbon dioxide, water and corresponding mineral acids. Of special interest is the decomposition of nitrogen oxides with a main focus on NO and NO_2. A review of the photocatalytic effectiveness for outdoor applications is not always possible due to the simultaneous variation of other parameters, such as traffic density and weather conditions. Therefore, for the simulation of air pollutants numerical models for the release calculation in the atmosphere, the transport of pollutants in the gas phase, and the interaction with solid surfaces are used.

The determination of the deposition rate of available photocatalytic materials is currently limited to examining those embedded in matrices and formulations, e.g. for concrete surfaces, roof tiles or plaster, since these currently have the largest commercial proportion of photocatalytically active products. An evaluation of other, especially vacuum-based, coating processes for the deposition of TiO_2 layers has not yet taken place. To create a basic understanding of the essential process parameters influencing photocatalytic NO oxidation thermal atomic layer deposition is used.

In this work suitable process windows for the deposition of photocatalytic TiO_2 are identified and evaluated with a main focus on the precursor combinations $TiCl_4/H_2O$, $TiCl_4/O_3$, TTIP/H_2O, TTIP/O_3 and $TiCl_4$/TTIP. Process parameters affecting the crystallinity of the TiO_2 layers and thus the photocatalytic effectiveness and the process-related layer properties with different process temperatures and layer thicknesses are determined.

For a cross-method and unified comparison of the TiO_2 layer properties the photocatalytic oxidation of methylene blue in aqueous solution and the degradation of nitrogen monoxide in a photoreactor are compared with each other as well as the kinetic modelling which was observed and simulated during NO degradation.

AF-MoP-73 High Vacuum Chemical Vapour Deposition: High Growth Rate ALD-Like Film Synthesis and Epitaxial CVD for Integrated Photonics

***Wojciech Szmyt**, J. Geler-Kremer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *S. Abel,* Lumiphase AG, Switzerland; *J. Fompeyrine,* Lumiphase, AG, Switzerland; *P. Hoffmann,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

In high-vacuum chemical vapour deposition (HV-CVD), heated substrates are exposed to continuous precursor fluxes from orifices in the precursor delivery system. Owing to the HV conditions, the precursor trajectories are ballistic, therefore the fluxes can be evaluated analytically. By blocking of individual effusion orifices, a range of different combinations of precursor fluxes can be explored in a single synthesis, which vastly accelerates the process optimization for the desired film properties. This approach is referred to as combinatorial deposition.

Moreover, due to HV conditions the probability of gas-phase collisions between precursor molecules is negligible, and thus, the chemical reactions occur strictly on the substrate surface. This characteristic allows for ALD-like synthesis of the films at a higher growth rate than ALD, provided that the substrate temperature is below the pyrolysis threshold of the precursors. In one of the previous works of our group (Reinke *et al*., J. Phys. Chem. C, 2015, 119, 50, 27965–27971), we presented HV-CVD of TiO_2 using ALD precursors TTIP and H_2O at typical ALD temperatures 175-225°C, achieving growth rates of up to 2nm/min. The growth was demonstrated to follow ALD chemistry and kinetics. The combinatorial HV-CVD allowed to extract a range of kinetic parameters of the precursor system under study, thus proving the HV-CVD highly valuable as a tool for the fundamental study of ALD processes. Moreover, it shows that ALD processes can be adapted in the HV-CVD system for higher growth rates.

Owing to the negligible gas-phase reactions, in the CVD mode of HV-CVD, highly crystalline films are attainable. The HV-CVD-grown films rival the quality of molecular beam epitaxy results, achieved at lower temperatures, and providing much-improved process scalability and cost-efficiency. Our recent efforts have been focused on the epitaxial growth of $BaTiO_3$ on $SrTiO_3$-buffered substrates for integrated electro-optical devices using $Ba(iPr_3Cp)_2$, TTIP and O_2 as precursors (Borzì *et al*, Materialia, 2020, 14, 100953). Employing the combinatorial mode of growth, we have established the optimal precursor fluxes for the correct stoichiometry, validated by Rutherford backscattering and Elastic recoil detection elemental analysis. We also demonstrated the films to be epitaxial by XRD as well as <0.5nm root mean square roughness, as shown by AFM, both of which being crucial for the application.

ALD Fundamentals
Room Van Eyck - Session AF-TuM2
Simulation, Modeling, and Theory of ALD II

Moderators: Simon Elliot, Schrödinger, Inc., Michael Nolan, University College Cork

10:45am **AF-TuM2-1 Theoretical Understanding on the Chemical Principles of Atomic Layer Deposition***, **Bonggeun Shong**,* Hongik University, Korea (Republic of) **INVITED**

Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limiting surface reactions. Through ALD, exceptional conformality on high-aspect ratio structures, thickness control at the Angstrom level, and tunable film composition are achievable. Furthermore, area-selective ALD (AS-ALD) has recently emerged as a possible alternative bottom-up approach for nano-patterning. With these advantages, ALD is gaining interest as a powerful tool for many industrial and research applications, especially in microelectronic fabrication. Since the entire ALD process should be based only on the surfaces of the substrates, it is important to understand the surface chemical reaction mechanisms during ALD, in order to improve the process conditions and material quality of ALD. With development of modern simulation tools, utilization of quantum mechanical calculation is becoming increasingly useful toward deeper understanding and design of such chemical reactions. In this talk, fundamental principles governing the surface chemistry of ALD processes will be discussed. Especially, the talk will focus on the recent examples that theoretical analysis of various surface reactions together with experimental approaches could be synergistically enhance the research and development of ALD.

11:15am **AF-TuM2-3 A Study of Area-Selective TiO_2 Deposition Using First Principles Based Thermodynamic Simulations***, **Yukio Kaneda**,* Sony Semiconductor Solutions Corporation, Belgium*; E. Marques,* Katholieke Universiteit Leuven, Belgium*; S. Armini, A. Delabie, M. Setten, G. Pourtois,* IMEC, Belgium

Recent transistor developments consider not only dimensional scaling but also design device structures in the vertical direction to reduce the active footprint. Consequently, the structures and process steps are becoming increasingly complex. In that context, area-selective deposition (ASD), which enables film formation from the bottom-up in a specific area, has been attracting attention. In this field, a lot of work aims to improve selectivity and to increase the material variations that make ASD possible to suit the different target applications [1]. Understanding the atomic-scale physics and chemistry during ASD processes is essential for interpreting the results, as well as for enabling further developments and new applications.

Here, we propose a simulation technique to analyze chemical reactivities based on first-principles calculations and statistical thermodynamics as a method to gain insight into atomic-scale physics. In this framework, we will show how we can investigate the effects of chemical reactivity, and hence selectivity, on many chemical species and process conditions.

In this presentation, we report the results of the analysis performed on the ASD of TiO_2 on substrates patterned with end groups including OH and alkyl-silyl groups. First, we evaluated our method by comparing with experimental results of TiO_2 ALD using $TiCl_4$ and $Ti(OMe)_4$ as precursors, whose selectivity was already confirmed [2]. The theoretical results demonstrate better selectivity with $TiCl_4$ as precursor, consistent with experiment. The impact of the process temperature and purge times during ALD was also qualitatively consistent with the experimental results. Moreover, the theoretical results also indicated that the mechanism of selectivity degradation may be due to the desorption of inhibitors during ALD at the higher process temperature. Therefore, we used this technique to investigate whether the precursors and coreagents referred in [3] and inhibitors with altered ligand size, which are the end groups of the non-growing surface, are effective in improving the selectivity. In conclusion, we confirmed that the best performance had been obtained by combining $TiCl_4$ as a precursor and trimethylsilyl termination as an inhibitor.

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11:30am **AF-TuM2-4 Chemistry of Plasma Enhanced Atomic Layer Deposition of Co using CoCp2 and Nitrogen/Hydrogen Plasma***, **Ji Liu**, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

The copper interconnect issue that has arisen with the downscaling of semiconductor devices is a major challenge in the nanoelectronics industry. One solution is to find alternate materials that do not suffer these issues to replace Cu. Transition metal cobalt has attracted much attention due to low resistivity, particularly at small dimensions, and good physical and chemical stability. The deposition of metals onto the typical high aspect ratio structures in nanoelectronics devices is difficult and the atomic layer deposition (ALD) is applied due to the resulting conformality and precise thickness control at the atomic scale. Plasma-enhanced ALD (PE-ALD) is used for low-temperature thin film growth by alternating exposures of metal precursors and plasma reactants. The PE-ALD of Co has been experimentally investigated using Cp-based precursors. However, the reaction mechanism is not clear and theoretical studies on the reaction mechanism is entirely lacking.

In this presentation, we study the PE-ALD growth of Co by first principle calculations. The following central questions will be addressed: (Q1) what is the coverage and stability of the NH_x-terminated Co surfaces? The (001) surface, with a hexagonal structure, is the most stable and the (100) surface with a zigzag structure is less stable but has high reactivity. These two surfaces allow the study of the influence of the surface facet. The surface NH_x saturation coverage is studied by considering co-adsorption of NH and NH_2 terminations on both surfaces. (Q2) What is the reaction mechanism for the elimination of Cp ligands in $CoCp_2$ on these NH_x-terminated Co surfaces? A plausible reaction pathway includes: precursor adsorption, hydrogen transfer, CpH formation and desorption. The barrier for hydrogen transfer is calculated and the results show that (100) surface has higher activity than (001) surface. The final terminations after metal precursor pulse are determined. (Q3) What is the role of plasma radicals in the plasma cycle? Here, we focus on two parts: (1) how the remaining Cp ligands and surface NH_x terminations are eliminated with plasma generated radicals N_xH_y; and (2) how the metal surface is recovered with NH_x terminations at the post-plasm stage. Our DFT results highlight the importance of NH_x species to deposit high-quality and low-impurity Co thin films.

11:45am **AF-TuM2-5 Adsorption Mechanics of Trimethyl Metal Precursors on AlN, GaN and InN***, **Karl Rönnby**, H. Pedersen, L. Ojamäe,* Linköping University, Sweden

Aluminum nitride (AlN), gallium nitride (GaN) and indium nitride (InN), collectively known as the group 13 nitrides (13Ns), are important materials in many semiconducting applications, for example in optoelectronics as the range of band gaps, 6.3 eV for AlN to 0.7 eV for InN, ranges from UV to IR.

The standard ALD approach for growth of 13Ns is to use a trimethyl metal (TMMe, Me=Al, Ga or In) precursor together with ammonia as co-reactant. Although similar to the typical ALD process of Al_2O_3 from TMA and water, the growth of the 13Ns is much more challenging. This can be attributed to a much lower reactivity of nitrogen compared to oxygen. The badly tuned chemistry is evident by the non-stoichiometric ratios between the precursors in continuous CVD and the need to utilize plasma-enhanced processes, especially for InN, to achieve good growth rates. Theoretical investigations into the growth mechanism would yield a possibility to understand the limitations and apply targeted improvements to the process.

In this work, we modeled the adsorption mechanisms of the TMMe precursor by density functional theory (DFT) on a periodic surface slab. TMMe molecules were placed in proximity to possible adsorption sites and their structures were optimized. Further surface decomposition mechanisms were then explored. Transition states along the reaction paths were investigated by the nudge elastic band method (NEB). Investigations of the lateral interactions between adsorbed precursor molecules were performed by introducing multiple molecules into the simulation cell. A kinetic model was then derived, showing how the surface evolve over time during the metal pulse.

When introduced to a NH_2-terminated surface, the first TMMe precursor adsorbs by forming a Lewis adduct to a surface NH_2 group by donating its empty p-orbital to the electron pair on the surface nitrogen. From this position, the adsorbed precursor could decompose, reaching an end state with all methyl ligands removed. A second TMMe shows preferred adsorption close to an already adsorbed metal atom, indicating a nucleation effect. As not enough hydrogen atoms are cleared by the absorbing molecules, the surface will reach a saturation at a much lower coverage than 1 ML.

We also investigate how the different rates of adsorption, diffusion, and decomposition affect the separation of initial nucleation points and the rate of cluster growth during the ALD half-cycle.

ALD Fundamentals
Room Van Eyck - Session AF1-TuA
Characterization I

Moderators: Jan-Willem Clerix, Imec , Aile Tamm, University of Tartu

1:30pm **AF1-TuA-1 Reaction Mechanisms of ALD of Transition Metal Oxides from Metal Amido Complexes and Water***, **Giulio D'Acunto**, R. Timm, J. Schnadt,* Lund University, Sweden

Atomic layer deposition (ALD) is an outstanding deposition technique to deposit highly uniform thin films with atomic precision. In particular, ALD of transition metal oxide layers from metal amido complexes and water finds its way in several technological fields, including green energy devices and the semiconductor industry. These ALD reactions are believed to follow a reaction scheme based on the ligand exchange mechanism. The first half cycle of ALD of HfO_2, via tetrakis-dimethylamido hafnium and water, is expressed, according to the ligand exchange scheme, by the following equation: $HfL_4 + nS\text{-}(OH) \rightarrow S\text{-}O_n\text{-}HfL_{4\text{-}n} + nLH$, where S stands for surface and L for the amido ligand of the metal precursor.

Here, the surface S is supposed to play a largely passive role, and it is that it is hydroxylated. L remains chemically unchanged during the reaction. To address whether the model is correct or not, we employed time-resolved *in situ* and *operando* ambient pressure X-ray photoelectron spectroscopy (APXPS) during the ALD of HfO_2 on InAs covered by a thermal or native oxide, TiO_2, and SiO_2.

We find that the classic ligand exchange reaction mechanism does not describe the reaction path in any of the investigated sample systems. In particular, we find that ALD of HfO_2 on SiO_2 follows a bimolecular reaction mechanism based on the insertion of a β-hydride of one of the ligands in an amido complex dimer into the bond between another ligand and of the Hf ions in the dimer. As a result of its bimolecular nature, this reaction can take place only at sufficiently high coverage of physisorbed complexes on the SIO_2 surface. On TiO_2 we find that the early stage of the reaction is based on dissociative adsorption, followed by mono- or bi-molecular reaction paths, leading to the formation of new sets of surface species never identified in ALD reactions.

Moreover, for an easily reducible surface we find evidence of HfO_x formation already during the first ALD half-cycle due to the transfer of O atoms from the surface to the metal complex. Clearly, this contradicts the passive role of the surface in standard ALD models. Interesting, in the case of InAs covered by a thermal or native oxide, this phenomenon, which lies behind the so-called self-cleaning effect, guarantees a sharp interface between the III-V material and HfO_2, a prerequisite for next-generation MOSFETs.

Our results open new doors for improving devices based on ALD. Time-resolved *in situ* and *operando* APXPS allows us to follow the kinetics and mechanisms involved in ALD, in real time at second time resolution with significant benefit for the further improvement of our general understanding of ALD reactions.

1:45pm **AF1-TuA-2 An *in-Vacuo* X-Ray Photoelectron Spectroscopy Study of the Reaction of Trimethylaluminum With Water, Oxygen and Argon Plasma for Low Temperature Atomic Layer Deposition***, L. Cao, **Jin Li**, M. Minjauw, J. Dendooven, C. Detavernier,* Department of Solid State Sciences, Ghent University, Belgium

Low temperature atomic layer deposition (ALD) has been drawing great research interest because of its capability to coat on heat-sensitive substrates, such as flexible devices, polymers and biological materials. As a process with widespread applications, the surface chemistry of Al_2O_3 ALD at low temperature is still under extensive investigation.[1,2] In this work, the growth of Al_2O_3 using trimethylaluminum (TMA)/water and TMA/O_2 plasma have been investigated with *in vacuo* X-ray photoelectron spectroscopy (XPS) in the temperature range from 60 to 300 °C. Samples are transferred back and forth between the ALD chamber and the XPS analytical chamber without vacuum break to analyze the surface chemical state after each reactant exposure, providing insight into the evolution of surface species.

Our results confirm that the low temperature TMA/water process undergoes an incomplete surface reaction during the water exposure (Figure S1), resulting in a low growth per cycle of 0.66 Å/cycle at 60 °C. Persistent -CH_3 groups are present on the growth surface after the water exposure and its concentration increases with reducing temperature, in accordance with previous reports.[1,2] In spite of the continuous presence of surface -CH_3 groups during the whole process, the C impurity concentration in the film is found to be surprisingly low. XPS depth profiling showed that C only exists at the very surface region, and is not incorporated into the film (Figure S2). According to *in situ*spectroscopic ellipsometry data, the growth at low temperature still displays a linear growth behavior (Figure S3). Our results indicate that, although the reaction during one water half cycle is incomplete at lower temperature, the next few water half cycles tend to finish the job and no carbon is built into the film. In contrast, oxygen plasma can combust all carbon ligands regardless of the surface temperature (Figure S1), boosting the growth rate to 2 Å/cycle at 60°C. To further explore the power of plasma for low temperature ALD, a three-step TMA/Ar plasma/H_2O process is also investigated. The Ar plasma is found to change the Al–CH_3 surface groups into an intermediate product that can react more easily with H_2O to allow a more complete reaction, increasing the growth rate from 0.66 Å/cycle to 1.1 Å/cycle at 60°C while avoiding potentially damaging effects on sensitive substrates caused by the chemically active O_2 plasma.

[1] V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. **108**, 1 (2016).

[2] Z. Jin, S. Lee, S. Shin, D.S. Shin, H. Choi, and Y.S. Min, J. Phys. Chem. C **125**, 21434 (2021).

2:00pm **AF1-TuA-3 *In Vacuo* Cluster Tool for Studying Reaction Mechanisms in ALD and ALE Processes***, **Heta-Elisa Nieminen**, M. Chundak, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Film growth during an ALD process is solely dependent on the chemical reactions on the substrate surface. Well-behaving surface chemistry enables the key qualities which make ALD a superior thin film deposition method. In addition, surface reactions define the outcome of each process and can set critical challenges on the process development and integration. For these reasons, studying the chemical reactions in the film growth is of utmost importance to fully understand the growth process and exploit the advantages ALD has to offer. Exactly the same applies to atomic layer etching (ALE) processes.

A new cluster tool in HelsinkiALD laboratory allows reaction mechanism studies on a wide variety of process chemistries without exposing the sample to ambient atmosphere. In this tool a commercial flow-type ALD reactor is connected directly to a set of ultra-high vacuum analysis techniques so that after interrupting the process at a selected point the substrate can be transferred *in vacuo* straight from the ALD reactor to surface analysis. The chemical composition of the surface including reaction intermediates can be precisely investigated after each precursor pulse individually. The resulting information will be beneficial for resolving the overall ALD and ALE mechanisms.

The cluster tool contains currently x-ray photoelectron spectroscopy (XPS), hard x-ray photoelectron spectroscopy (HAXPES), ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and temperature programmed desorption (TPD). The film growth can also be monitored *in situ* by a quartz crystal microbalance (QCM) and ellipsometer which are connected directly to the ALD chamber. As the system contains a flow-type ALD reactor, the mechanisms can be solved without compromising true ALD conditions. The system has been tested and the operation procedures optimized with TMA and H_2O for depositing Al_2O_3 at temperatures of 150 – 300 ˚C. The state of the surface was investigated by TPD and XPS after each precursor pulse. After the initial testing with this well-known process, new ALD and ALE chemistries will be studied in detail.

Funding from the Academy of Finland by the profiling action on Matter and Materials, grant no. 318913, the Doctoral Programme in Materials Research and Nanoscience (MATRENA) and the use of ALD Center Finland research infrastructure are acknowledged.

2:15pm **AF1-TuA-4 Watching the ALD of Pt Films in Real-Time***, **Esko Kokkonen**,* Max IV Laboratory, Sweden*; M. Kaipio, H. Nieminen,* University of Helsinki, Finland*; F. Rehman,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; M. Putkonen, M. Ritala, S. Huotari,* University of Helsinki, Finland*; J. Schnadt,* Lund University, Sweden*; S. Urpelainen,* University of Oulu, Finland

We have used in situ and operando techniques to study the growth of Pt films on different substrates in real-time. In this study, we have focused on investigating the growth of metallic Pt on Si, Ir, and Ir oxide substrates. The precursors for this reaction were chosen as trimethyl(methylcyclopentadienyl)platinum(IV), or $MeCpPtMe_3$ and O_2 gas.

The experiments were done using the so-called ALD cell, which is an synchrotron-based ambient pressure X-ray photoelectron spectroscopy (APXPS) sample environment specifically dedicated for studies of ALD processes. The system is located on the SPECIES beamline [1] at the MAX IV Laboratory in Lund, Sweden. With a wide energy range of 30-1500 eV, the beamline offers wide measurement capabilities for both core-level XPS as well as valence band (ultraviolet photoelectron spectroscopy) UPS using surface sensitive photon energies. This setup has been recently used in several studies to gain deeper insight into different ALD processes [2, 3].

We have followed various core-levels on the surface using XPS as it was exposed to the first half-cycle with the $MeCpPtMe_3$ precursor. Interesting effects are seen on the three different substrates. Firstly, the Pt 4f core-level shows a clear intensity increase, naturally following from the addition of Pt containing precursor onto the surface. However, an interesting finding is that for all substrates, the Pt 4f binding energy shifts during the deposition. Moreover, the shifting of the Pt 4f peaks occur at a different timescale than the saturation of the surface based on the XPS intensity. A tentative explanation could be that the Pt precursor initially attaches to the surface with a higher oxidation state, perhaps still partially attached to some of the methyl groups, which rather quickly dissociate (or combust) and are released into the gas phase. This mechanism then could be on-going while the surface is only partly covered by the Pt since saturation is not yet reached.

[1] E. Kokkonen, et al. "Upgrade of the SPECIES beamline at the MAX IV Laboratory." *Journal of Synchrotron Radiation***28**, 2, 588-601 **(2021)**, DOI: 10.1107/S1600577521000564
[2] G. D'Acunto, et al. "Oxygen relocation during HfO_2 ALD on InAs." *Faraday Discussions* Accepted Manuscript (2022). DOI: 10.1039/D1FD00116G
[3] E. Kokkonen, et al. "Ambient pressure x-ray photoelectron spectroscopy setup for synchrotron-based in situ and operando atomic layer deposition research." *Review of Scientific Instruments* 93.1, 013905 (2022). DOI: 10.1063/5.0076993

2:30pm **AF1-TuA-5 In Situ X-Ray Studies of Lamellar Dichalcogenides Prepared by Molecular Layer Deposition and Thermal Annealing***, **Petros Abi Younes,*** CEA/LETI-University Grenoble Alpes, France*; E. Skopin,* LTM - MINATEC - CEA/LETI, France*; M. Zhukush, C. Camp,* Univ. Lyon, CNRS-UCB Lyon 1, France*; N. Aubert , G. Ciatto,* Synchrotron SOLEIL Beamline SIRIUS, France*; N. Schneider,* UMR-IPVF, CNRS, France*; M. Richard,* ESRF, France*; N. Gauthier,* CEA/LETI-University Grenoble Alpes, France*; E. Quadrelli,* Univ. Lyon, CNRS, France*; D. Rouchon,* CEA/LETI-University Grenoble Alpes, France*; H. Renevier,* Laboratoire des Matériaux et du Génie Physique, France

Metal Dichalcogenides **(MDs)** have recently emerged as a class of exceptional materials with many potential applications and are receiving great attention. Among them, lamellar Titanium disulfide (**TiS_2**) is the lightest and cheapest member of the Transition MDs(**TMDs)** family,[1]with a $1T\text{-}TiS_2$ crystallographic structure. Its electrical properties allow it to use in many fields of applications (optics, thermoelectric, and batteries).[2–5]

However, the lack of scalable fabrication methods of continuous ultra-thin films on developed surfaces, at moderate temperature, stems a sizeable bottleneck for the full deployment of these materials. Besides the conventional Atomic Layer Deposition (ALD) process, which suffers from limitations, an innovative **2-step process** comprising Molecular Layer Deposition (**MLD**) and **thermal annealing** has been developed to achieve an atomically-thin synthesis of 2D TMDs MoS_2 and WS_2.[6,7] Interestingly, the process does not use the highly toxic H_2S molecule. By using this approach we have succeeded to synthesize continuous and textured TiS_2 thin films on thermal SiO_2[8]. An intermediate amorphous polymer (Ti-thiolate) is deposited by MLD at low temperature (T_{sub} = 50°C) upon a reaction between the metal precursor (TDMAT = $Ti(NMe_2)_4$) and organic sulfide molecule (1,2-ethanedithiol). Then, the amorphous thin film undergoes a thermal annealing under hydrogenated argon flow.

Both the MLD and thermal annealing were monitored by *in situ* synchrotron radiation techniques, including x-ray fluorescence (XRF), x-ray reflectivity (XRR), and x-ray absorption fine structure (XAFS), at SIRIUS beamline (SOLEIL, St Aubin), and *in situ* ellipsometry. The main results will be presented. Importantly, both the sulfur K and Ti K fluorescence line intensities could be recorded simultaneously, allowing us to monitor simultaneously the S and Ti contents throughout the whole process and from the very early stage of the Ti-thiolate deposition. The repetitive self-limiting growth behavior during the MLD step could be demonstrated. Upon thermal annealing, the Ti-thiolate thin film transforms into lamellar TiS_2 monolayers parallel to the substrate surfaces observed by Raman spectroscopy, transmission electron microscopy (TEM) and x-ray linear dichroism at the Ti K-edge. Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) and lab-scale Hard XPS (HAXPES) show stoichiometric TiS_2 in the presence of carbon.

References

[1]*Nano Today***2014**,*9*,604; [2]*Nano Lett.***2018**,*18*,4506; [3]*Phys. Rev. B***2019**,*99*,165122; [4]*Photonics Res.***2018***6*,C44; [5]*Phys.Chem.Chem.Phys.* **2012**,*14*,15641; [6]*Nanoscale***2017**,*9*,538; [7]*JVST A.***2017**,*35*,061502. **[8]Chem Mater 2022 (submitted)**

2:45pm **AF1-TuA-6 *In Situ* Spectroscopic Ellipsometry of 3D Patterned Nanostructures for Real Time Profile Evolution During ALD***, **S. Novia Berriel,*** University of Central Florida*; N. Keller,* Onto Innovation*; P. Banerjee,* University of Central Florida

In situ techniques are used to gain understanding of ALD processes in real time. In nearly all cases, planar substrates are used to monitor surface reactions and film growth. However, since ALD is used for conformal deposition in high-aspect ratio structures, the use of in situ techniques on planar substrates present a challenge in interpreting deposition characteristics on non-planar substrates and optimizing processes which can lead to conformal growth of ALD films inside high-aspect ratio structures.

In this talk, we will describe an optical-based metrology technique to monitor real time growth of ALD ZnO on patterned SiO_2 nano trenches. The primary advantage of this technique is that our hardware remains a spectroscopic ellipsometer (SE), whereas back-end data analysis and modeling is conducted using a rigorous coupled-wave analysis (RCWA) technique.

Patterned SiO_2 trenches with a width of 80 nm and a depth of 325 nm were used as substrates. Real-time polarization data (Ψ and Δ) were obtained across two runs – one, in which the trenches were parallel; and two, in which the trenches were perpendicular to the beam path. The profile evolution of ALD ZnO was monitored for 300 cycles, corresponding to a thickness of 55 nm on planar substrates. RCWA of the polarization data was used to generate 3D cross-section profiles of the SiO_2 trenches filling with ZnO from the beginning to the end of deposition.

The film thicknesses at various points along the trench and the resulting conformality were confirmed using cross-section SEM analyses. We find that RCWA is successfully able to predict thickness to within 7.8% and conformality to within 8.1% of true experimental data. Furthermore, the RCWA predicts the merging of growth fronts at the bottom of the trench in accordance with geometrical modeling and experimental observations. These promising results highlight the potential for real-time monitoring of in-trench conformality via a combination of SE and RWCA techniques

3:00pm **AF1-TuA-7 Pyroelectric Calorimetry: Measuring the Time-Resolved Heat of ALD Half Reactions***, **Ashley R. Bielinski,** A. Martinson,* Argonne National Laboratory **INVITED**

In Situ characterization methods provide insight into ALD reactions as they occur.We've implemented pyroelectric calorimetry as an *in situ* technique to measure the heat evolved in ALD half reactions with unrivaled thermal and temporal resolution.On high surface area substrates like nanoparticles or metal organic frameworks, ALD has been observed to cause temperature increases greater than 10°C.The small temperature changes (<0.1 °C) predicted for planar substrates are more challenging to accurately measure.We designed custom pyroelectric calorimeters for implementation in an ALD tool with thermal and temporal resolution down to 0.1 $\mu J/cm^2$ and 50 ns.To put this in perspective, this corresponds to a temperature increase of about 10^{-5}°C, which is less than 0.1% of the heat evolved in the reaction between trimethylaluminum (TMA) and water.The calorimeter response time is more than 10^4 times faster than our measurement of the reaction time of TMA on a hydroxylated alumina surface.

Analysis of time resolved heat generation in ALD reactions provides information on thermodynamics and kinetics as well as how real reactions deviate from simplified textbook examples.Experimental reaction heats can be compared with theoretical and computational predictions of the interaction between specific precursors and surface sites, showing which of the hypothetical pathways best represent reality.Additionally, pyroelectric calorimetry is orders of magnitude faster than many complementary *in situ* analysis techniques, providing more granular insight and subdivision of individual half reactions.

We've combined pyroelectric heat generation analysis with *in situ* spectroscopic ellipsometry in a saturation study of the prototypical reaction between TMA and water.This represents the most accurate measurement to-date of ALD reaction heats.Comparison between these parallel *in situ* measurements provides insight into the reaction energy as the surface saturates within a single half reaction and the time-resolved data highlights the limitations of slow water reaction kinetics.In addition to fundamental studies of ALD surface reactions, careful analysis of heat transfer due to precursor flow can provide information on precursor delivery and flow dynamics within the ALD reactor.

The development of pyroelectric calorimetry for ALD provides many opportunities for future investigations.Of particular interest are applications requiring sub monolayer detection such as precursor reactions with specific surfaces sites in area or defect selective ALD as well as time-resolved kinetics studies.

ALD Fundamentals
Room Van Eyck - Session AF2-TuA
Characterization II

Moderators: Bart Macco, Eindhoven University of Technology, Juan Santo-Domingo Peñaranda, Ghent University, Belgium

4:00pm **AF2-TuA-11 Get the Full Picture: Full-Range Time-Resolved In Situ Mass Spectrometry During ALD*, Andreas Werbrouck*,** *J. Dendooven, C. Detavernier,* Ghent University, Belgium **INVITED**

In situ measurements are indispensable for developing, characterizing, and understanding ALD processes. Quadrupole mass spectrometry (QMS) is one technique available to monitor the gas mix in the reactor (or at the exhaust) while surface reactions are ongoing. In QMS, gas from the reactor is sampled, ionized, and fragmented. These fragments have specific mass-to-charge ratios, and their relative intensities provide a way to fingerprint the chemical species present. However, typical tools can only detect a single mass at a time, leading to poor time resolution. Additionally, the generated reaction products may be complex, unexpected, and as they are generated by a self-limiting surface reaction, they are only present in the reactor for a limited amount of time.

Here, we propose a way to exploit the cyclic nature of ALD, collecting QMS data over multiple cycles in order to collect a full-range, time-resolved picture of the gas mix in the reactor during an ALD process. This allows to effectively bypass the limitations of traditional QMS during ALD with only minimal hardware changes to the reactor. Over the past years, we have used this technique to investigate the archetypal TMA-water process and detected a secondary reaction product for water, to study the deposition of lithium-containing films, and to study the deposition of ruthenium dioxide.

In the first part of the presentation, the data collection and post-processing routines will be clarified. The second part of this talk will handle specific use cases, and the tools that can be used to make sense of the large amount of collected data will be discussed. Time-resolved, full-range quadrupole mass spectrometry measurements may be indispensable to get the full picture of your atomic layer process.

4:30pm **AF2-TuA-13 Strategies to Produce Boron-Containing ALD Thin Films Using Trimethyl Borate Precursor: From Thermal to Plasma to Combined-Plasma Approach*, Arpan Dhara,*** *A. Werbrouck, J. Li, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Recent research takes interest in boron-comprising thin layers that are useful in many applications such as dopant for semiconductors, neutron detection and absorption layer in nuclear reactors, ceramic reinforcements, and lithium ion batteries. The most fundamental boron-containing layer, $B_2O_{3,}$ is highly hygroscopic, and therefore ternary oxides (like $Al_xB_yO_z$) or B-doped oxide (like ZnO:B) are more commonly prepared, using a so-called ALD supercycle approach. Generally, the boron concentration in these films is unequivocally poor (~1-10%) when the metal oxide to boron oxide cycle ratio is 1:1. Stoichiometric films are obtained only from a particular (pyrazolyl) type of precursor, however the high vaporization temperature (~200°C) hampers their practical use. Therefore, there is a need of finding a suitable precursor and convenient process to produce boron-containing thin films.

In this work, we demonstrate different strategies (figure 1) to produce aluminium borate thin films by ALD using trimethyl borate (TMB) as the boron source. Films obtained from *thermal* processes (***TMA-H_2O-TMB** or* ***TMA-H_2O-TMB-H_2O***) show a moderate growth per cycle (GPC, 0.85 & 1.5 Å respectively), and contain considerable carbon impurities. Also, a constant increase in growth rate is observed with temperature which suggests a low reactivity of the TMB molecule. The reactivity can be improved by using oxygen plasma (***TMA-$O_2{*}$-TMB-$O_2{*}$***) instead of H_2O as O source. The GPC certainly improves a bit (~1.8 Å) along with a reduction in carbon contamination. However, the boron concentration in the films remains very low for the investigated processes (~5-10%).

To improve the growth rate and boron concentration further, we introduce a novel approach where a combination of H_2O and TMB is used in plasma form (**TMA-[TMB+H_2O]${*}$**). It is proposed that the TMB molecules ***polymerize in-situ*** in the plasma, as reported before for trimethyl phosphate plasma.[1] However, using TMB alone in plasma form does not yield self-limiting ALD growth, as polymerized species continuously accumulate on the substrate. Interestingly, by adding H_2O to the TMB plasma, saturated growth of aluminium borate films is achieved with a high GPC of ~3.5 Å/cycle. Moreover, the films contain a considerably larger amount of boron (~15-20%). We hypothesize that H_2O in the TMB plasma helps to hydrolyse surface groups, which in turn aids in preventing continuous polymerization. We also performed ***time resolved transient in-situ mass spectroscopy*** (figure 2) and ***in-vacuo XPS*** studies to reveal the mechanism of all three different approaches explained above.

1. T. Dobbelaere et. al., *Chem. Mater.***26**, 6863–6871 (2014)

4:45pm **AF2-TuA-14 Examining Large Grain Growth and Low Temperature Crystallization Kinetics for TiO_2 Thin Films Prepared by Atomic Layer Deposition (ALD)*, Jamie Wooding,*** *K. Kalaitzidou, M. Losego,* Georgia Institute of Technology

This presentation will describe an atomic layer deposition (ALD) process to prepare large crystal anatase TiO_2 thin films (>1 micron at <100 nm thickness) and provide a roadmap to determine fundamental crystallization kinetics quantities for thin film systems. Films are deposited using tetrakis(dimethylamino)titanium(IV) (TDMAT) and water at 140 °C and 160 °C, followed by an *ex situ* low-temperature post-deposition anneal (PDA) from 140–200 °C. All as-deposited thin films are amorphous by X-ray diffraction (XRD) and Raman spectroscopy. During the post-deposition anneal, the crystallization process is tracked via scanning electron microscopy (SEM). As depicted in Figure 1, these low anneal temperatures achieve large grain growth resulting in crystal sizes of 0.8–1.2 µm in lateral dimension for a film thickness of 50 nm. The time-dependent transformation fraction is fit to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model (Figure 2a), which reveals a continuous nucleation process and a two-dimensional growth mechanism, consistent with the observed large grains.Crystal nucleation rate is observed for short annealing times to determine the critical free energy for anatase nucleation and then combined with the transformation reaction rate from the JMAK equation to determine the activation energy for grain growth (Figure 2b). The energy required for nucleation of 1.32–1.35 eV K^{-1} $atom^{-1}$ is an order of magnitude greater than the activation energy for grain growth of 0.12–0.24 eV K^{-1} $atom^{-1}$; as such, nucleation has the more significant energy barrier at these lower temperatures. Films deposited at 160 °C have higher nucleation rates than those deposited at 140 °C despite both films having comparable critical free energies for nucleation. These greater nucleation rates originate from an increased nucleation frequency factor (Figure 2b), indicating improved mobility or a higher degree of proto-nuclei. Using this TiO_2 large grain crystal growth study as a prototype, this work demonstrates a method to predict post-deposition crystallization behavior in ALD thin films.

5:00pm **AF2-TuA-15 Deposition and Characterization of Hafnium Dioxide Films Embedding Nickel Nanoparticles*, Markus Otsus,*** *J. Merisalu, T. Viskus, T. Kahro, A. Tarre, K. Kalam, A. Kasikov, P. Ritslaid, J. Kozlova, K. Kukli, A. Tamm,* University of Tartu, Estonia

Controlled defects introduced in nanolaminates designed for use in resistive switching devices can improve the overall performance of memristors. Nanoparticles (NP) can guide the process of conductive filament formation thus lowering voltage and enhancing stability of resistive switching [1]. As overall the density of conductive filaments is low, observations of conductive filaments in or around a NP with scanning transmission electron microscopy (STEM) imaging could be possible. Studying the filaments shape and composition with STEM imaging and energy dispersive X-ray spectroscopy (EDS) analysis may allow us to better understand the process and mechanism of their formation [2].

Resistive switching properties of four different structures were examined. The aim was to produce otherwise similar structures (Figure 1) with and without Ni-NPs, using two different precursor systems at the same substrate temperature (220 °C), $HfCl_4$ +O_3, and tetrakis(ethylmethylamino)hafnium (TEMAH) + O_2 plasma, and two different atomic layer deposition (ALD) reactors – a flow-type in-house built hot-wall reactor and a Picosun R200 Advanced System, respectively. Starting with a Si(100) planar wafer substrate covered with a conductive TiN film, a two-step ALD process was used to embed the nickel NPs in-between a HfO_2 layer. Following the deposition of the dielectric layer, titanium top electrodes were produced using maskless photolithography and electron beam evaporation.

Scanning electron microscopy (SEM) showed the NPs uniformly dispersed across the sample area, apart from a few clusters observed. Current-voltage measurements were carried out, and in the samples with NPs, lower voltages were needed to switch between high-resistive state (HRS) and low-resistive state (LRS) (Figure 1), compared to the particle-free samples. SEM-focused ion beam was used to produce lamellas from films with and without Ni-NPs, which were then analyzed with STEM and EDS to evaluate the composition and uniformity of the layers (Figures 2 and 3). Nanocrystals were monitored in HfO_2 grown from TEMAH, while the $HfCl_4$ based oxide layer appeared structurally homogenous. Conclusively, electrical and microscopy findings were compared and a possible cause for the results observed was proposed.

[1] W. Banerjee, Q. Liu, and H. Hwang, “Engineering of defects in resistive random access memory devices,” *J. Appl. Phys.*, 127 (2020) 051101, doi: 10.1063/1.5136264.

[2] D.-H. Kwon *et al.*, “Atomic structure of conducting nanofilaments in TiO_2 resistive switching memory,” *Nat. Nanotechnol.*, 5 (2010) 148-153 doi: 10.1038/NNANO.2009.456.

5:15pm **AF2-TuA-16 Biased QCM for Studies of Reductive Surface Chemistry Induced by Plasma Electrons***, **Pentti Niiranen**, H. Nadhom, D. Lundin, H. Pedersen,* Linköping University, IFM, Sweden

Metallic films are an immensely important part of the modern world e.g., in a variety of applications such as sensors, catalysts, optoelectronics and nanoelectronics. For any ALD, or CVD, approach to metal films using a metal precursor with a positive valence, the fundamental surface chemistry is a reduction reaction. However, reduction of electropositive metals in ALD and CVD is especially difficult due to the shortage of precursors with the appropriate reduction power to overcome the thermodynamical disadvantage and complete the reduction. In a recent study, the electrons from a plasma discharge was used for the reduction of first-row transition metals (Co, Fe and Ni) in a CVD process, instead of using a co-reactant as a reduction agent.[1] By applying a positive bias to the surface, the plasma electrons were drawn to the substrate surface and facilitated metal growth. The process is also demonstrated to be inherently area-selective from the electrical resistivity of the substrate, depositing metal only on low-resistivity surfaces, leaving high-resistivity surfaces uncoated.[2] The surface chemical model for this process must be developed to understand and develop the method. As a first step to develop the surface chemical model, we here present a biased QCM system, capable of attracting plasma electrons to the QCM-head. Initial result shows the great potential of the modified QCM for the process where plasma electrons are used as reducing agents.[1] By using the biased QCM in combination with residual gas analysis and quantum chemical modelling we are building a surface chemical model of the process. The biased QCM-method can also aid us in our efforts to develop the method into a time-resolved method. We note from the QCM-curves that they suggest that self-limiting surface chemistry is possible using the new plasma electron based CVD method.

[1] Nadhom, et al. *J. Vac. Sci. Technol. A*, 2020, 38, 033402, 2020.

[2] Nadhom, et al. *J. Phys. Chem. Lett.*, 2021, 12, 4130.

5:30pm **AF2-TuA-17 NHC Monolayer Growth Behaviour and Film Durability Measured by QCM***, **Eden Goodwin**,* Carleton University, Canada*; A. Veinot, I. Singh,* Queens University, Canada*; P. Ragogna,* Western University, Canada*; C. Crudden,* Queens University, Canada*; S. Barry,* Carleton University, Canada

We have previously seen N-heterocyclic carbene (NHCs) containing gold precursors etch gold surfaces during quartz crystal microbalance (QCM) studies (Goodwin, AVS ALD 2021). Although we have proposed an etch mechanism, the role of the surface NHC remains unclear.

NHCs have been shown to reconstruct gold surfaces by dislocation and displacement of individual atoms on the surface and to bind to gold surfaces in several different conformations (upright, flat, in clusters) dependant upon their functionalization (Smith et al., 2019). The di-isopropyl NHC that was previously reported is expected to bind in an upright manner, a binding behaviour that can not be predicted and needs to be determined through scanning tunneling microscopy (STM) imaging on single crystal gold surface. Analyzing NHC binding behaviour this way has several downsides: cost of single crystal gold surfaces, availability of STM imaging facilities, and lengthy processing time. To alleviate these issues, we propose to quantify coverage and corroborate binding geometry by QCM studies. Additionally, we are investigating the effect of gold species ($AlCl_3$, (Me)AuNHC, $(Me)_3AuPMe_3$) on both the carbene monolayer and gold surface.

In this work we deposit a series of simple NHCs in a home-made tube furnace reactor using a 100-cycle pulse sequence (60s pulse, 20s N_2 purge) and subsequently expose these to gold-containing species. Real time high resolution (10 counts per second) surface analysis is done using a 6 MHz in-situ polished gold coated QCM crystal. Time resolved mass gain analysis is used to confirm saturative growth behaviour, determine the number of occupied gold sites, and to test film stability when exposed to a variety of Au species. A low resolution (<300 AMU) in-situ quadrupole mass spectrometer (QMS) is used to confirm the presence of free NHC and determine volatile products formed during surface decomposition or etch processes.

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