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 RuO₄ 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.

References:

1.   Ryden et al., *Physical Review B* **1970,** *1* (4), 1494.
2.   Austin et al., *Chemistry of Materials* **2017,** *29* (3), 1107-1115.

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: PbBr₂ and PbCl₂, *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.

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