ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-MoA
ALD Precursors I

Moderators: Daniel Alvarez, RASIRC, Charles H. Winter, Wayne State University

1:30pm **AF2-MoA-1 The Materials Supplier Challenge: Flawless Execution from Precursor Design to High Volume Manufacturing*, Madhukar B. Rao,*** Versum Materials **INVITED**

Advancements in scaling and architecture in logic and memory devices are driving the development of new precursors which provide more precise control of film thickness, composition, morphology and electrical properties. The challenge for materials suppliers is to design new precursors that can meet the performance requirements, and scale-up the precursors to high volume, while meeting the cost of ownership targets. At Versum Materials, the process starts with defining technical requirements of the precursor through close collaboration with the customer and equipment vendor. We use our in-depth understanding of the structure-property relationships between precursor and final film to identify and synthesize promising new precursors on the laboratory scale and rapidly test new precursors using our in-house deposition capabilities to confirm the film performance. These results are validated with our collaboration partners and this defines the potential candidates for further scale-up.

Converting promising laboratory discoveries into viable commercial products is a complex and resource-intensive effort. The product development work must scale up and validate a low-cost synthetic route and purification methods, identify and quantify EH&S risks (e.g., toxicity, stability, reactivity), develop analytical methods to fingerprint incoming raw materials and ensure final product quality, design and validate suitable containers for delivery, ensure supplier quality and supply-chain readiness and prepare for container life-cycle management. This presentation highlights the key steps and technical challenges in the product development process and highlights the importance of close collaboration with customers, suppliers, and equipment manufacturers to make new products HVM ready.

2:00pm **AF2-MoA-3 Precursor and Co-Reactant Selection: A Figure of Merit*, Seán Barry,*** *M Griffiths,* Carleton University, Canada

Developing novel precursors for atomic layer deposition (ALD) processes is a complicated task: the selected chemical compounds must be volatile and thermally stable, yet reactive with a surface, and perhaps even demonstrate selective reactivity among several different surfaces. Additionally, it is helpful if the precursors are liquid (for handling and to improve the kinetics of evaporation) and robust to a change in the chemical environment.

To initially study a compound for potential use as a precursor, one must understand both the volatility and thermal stability. We have recently established a Figure of Merit (FoM) for potential precursor compounds based on volatility and decomposition. Conceptually, this FoM alters the ratio in temperature between a judiciously chosen onset of decomposition and onset of thermolysis and modifies that with respect to the residual mass left behind in a standard thermogravimetric ramp experiment. In this way, the larger the value for the FoM, the better the precursor, with negative values representing compounds that decompose before acceptable volatility is achieved.

Selection of the onset of volatility and decomposition, as well as the construction of this Figure of Merit will be examined with respect to potential precursors for transition metals (Ni, Co, W, Mo, Au, Ag, Cu) as well as main group metals (Al, Ga, In, Sn, Pb) that are presently being developed in our group.

2:15pm **AF2-MoA-4 Designing Thermal Atomic Layer Deposition Processes for Gold Metal using New Organogold Precursors and Co-reageants*, Matthew Griffiths,*** *G Bačić, A Varga, S Barry,* Carleton University, Canada

Gold nanoparticles have been studied extensively by virtue of their plasmonic properties and their ability to act as photocatalysts for CO_2 reduction and hydrogenation. In 2016, our group showed that $(PMe_3)AuMe_3$ would deposit gold nanoparticles by atomic layer deposition (ALD) using oxygen plasma and water as co-reagents. Recently, Van Daele et al. showed that the same compound could deposit gold with hydrogen plasma as a co-reagent at temperatures as low as 50 °C. The development of a process that uses thermal co-reagents is ongoing in our laboratory in order to circumvent the use of harsh co-reagents.

Bimolecular reductive coupling is believed to catalyze the on-surface decomposition of $(PMe_3)AuMe$ on Au. Thus, increasing the steric bulk of the alkyl ligand should increase the activation energy of this process and produce a surface species that resists decomposition to metallic gold. We synthesized a series of $(PMe_3)AuR$ compounds (R = Me, CH_2SiMe_3, $CH(SiMe_3)_2$, and $C(SiMe_3)_3$) with a stepwise increase in steric bulk. We then developed a screening process to test their ability to form self-limiting surface monolayers with an *in situ* quartz crystal microbalance (QCM). At equal vapour pressures and equal deposition temperatures, the rate of CVD decreased with increasing steric bulk, but was never fully prevented.

N-heterocyclic carbenes (NHCs) are ubiquitous ligands in modern chemistry, and they also form robust self-assembled monolayers on gold. We envisioned a second strategy where an NHC ligand bound to Au(I) in the general formula (NHC)AuR could play the role of the self-limiting ligand in an ALD process. All that would be needed is a co-reagent which could remove the NHC from the metallic gold surface to complete the cycle. A series of alkylgold(I) NHCs were synthesized and tested with a focus on small alkyl groups and stable, sterically unhindered NHCs to facilitate efficient packing on the surface. Using our QCM methodology, we compared the various compounds for their ability to form self-limiting monolayers, and we analyzed the gas-phase products of the ALD reactions using *in situ* quadrupole mass-spectrometry (QMS).

Finally, exploration of a third strategy was initiated by our discovery that a thermally stable *N*-heterocyclic silylene (NHSi) reacted with our previously reported and stubbornly inert gold ALD precursor $(PMe_3)AuMe_3$. We identified a highly reactive silylgold(I) silylene species by solution-phase NMR spectroscopy and set out to develop an ALD process using these two compounds. The surface chemistry was studied using our combined QCM and QMS methodology, and the final film properties were evaluated *ex-situ* by 4-point probe, XPS, and XRD.

2:30pm **AF2-MoA-5 A New Carbene Based Silver Precursor Applied in APP-ALD Yielding Conductive and Transparent Ag Films: A Promising Precursor Class for Ag Metal ALD*, Nils Boysen,*** Ruhr University Bochum, Germany*; T Hasselmann, D Theirich, T Riedl,* University of Wuppertal, Germany*; A Devi,* Ruhr University Bochum, Germany

The realization of transparent electrodes for solar cells and light-emitting devices based on metals like silver still remains a challenge due to a preferred Volmer-Weber growth mode in the initial stages of thin film growth. This results in a typically observed metal island formation with a high sheet resistance (R_{sh}) at a low film thickness. Atomic layer deposition (ALD) can be the method of choice to effectively lower the percolation threshold and to afford electrically conductive but at the same time optically transparent silver thin films. While the influence of different reducing agents in thermally- and plasma-activated silver ALD processes was studied in the past, the employment of different silver precursors and their influence on the growth behavior and percolation threshold of silver thin films was not coherently studied before due to the limited number of volatile and thermally stable silver precursors. To overcome this issue and to set a starting point for further comprehensive studies, we herein report the synthesis and evaluation of a new fluorine-, oxygen- and phosphorous-free volatile N-heterocyclic carbene (NHC)-based silver precursor.[1] The successful synthesis of the new NHC-based silver amide compound 1,3-di-*tert*-butyl-imidazolin-2-ylidene silver(I) bis(trimethylsilyl)amide [(NHC)Ag(hmds)] was confirmed *via* ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis and EI-MS, while the thermal characteristics of the compound were determined *via* thermogravimetric and isothermal thermogravimetric analysis. Subsequently, the volatile silver precursor [(NHC)Ag(hmds)] was employed in spatial atmospheric plasma-enhanced ALD (APP-ALD) yielding high purity conductive silver thin films at temperatures as low as 100 °C and with a low resistivity of 10^{-5} Wcm utilizing an Ar/H_2 plasma. The growth characteristics were investigated, and the resulting thin films were analysed *via* SEM, XPS, optical transmittance (UV-Vis) and RBS. Compared to a nominally identical process employing the commercially available silver precursor [Ag(fod)(PEt_3)], [(NHC)Ag(hmds)] was able to considerably enhance the growth rate and prohibit unwanted contaminants like fluorine, oxygen and phosphorous. This renders the new precursor as a promising alternative to the currently established [Ag(fod)(PEt_3)]. The current study marks the first example of a carbene stabilized Ag complex that was successfully employed for ALD applications of Ag metal layers. In addition, these promising results create a basis for the development of new metal ALD precursors as there is only a very limited number of ALD precursors known, especially for silver metal ALD.

2:45pm **AF2-MoA-6 Transition Metal β-ketoiminates: A Promising Precursor Class for Atomic Layer Deposition of Binary and Ternary Oxide Thin Films***, **Dennis Zywitzki**, A Devi,* Ruhr University Bochum, Germany

Due to their abundancy in the earth's crust and promising characteristics in (photo-) electrocatalysis and energy storage devices, binary and ternary oxide films of first row transition metals such as Fe, Co, Ni, Zn have gained increasing attention in recent years. ALD is a promising technique for such applications, as it guarantees excellent interface quality to the underlying substrate and enables the conformal coating of large and nanostructured surfaces. Precursors for these metals however remain limited especially for water assisted processes. While ALD processes for ZnO are dominated by the pyrophoric alkyl compounds such as diethyl zinc, few other precursors were reported thus far. On the other hand, for Fe, Co and Ni, metal cyclopentadienyls and β-diketonates, which require strong oxidizing agents like ozone, have often been used. Water assisted process were realized by utilization of the amidinate ligand system for Fe, Co and Ni. In order to find a compromise between the stable but less reactive metal β-diketonates and the highly reactive metal β-ketiminates, metal β-ketoiminates have been found to be a promising precursor class, which can easily be tuned in terms of volatility and reactivity by employing different substitutions at the imino moiety.

A series of new β-ketoiminato precursors, suitable for ALD have been developed for transition metals. As representative examples, Fe, Co, Ni and Zn β-ketoiminates have been synthesized in good yields and were thoroughly characterized with regard to their purity, composition and molecular structure by NMR spectroscopy, elemental analysis, EI-MS and single crystal XRD. The spectroscopically pure and monomeric compounds were reactive toward water. Their volatility and decomposition behavior was evaluated by thermal analysis and were found suitable for ALD. The introduction of etheric sidechains led to lower melting points, ensuring a steady evaporation rate. Subsequently, water assisted ALD processes with Fe and Zn β-ketoiminate precursors were developed. The typical ALD characteristics were confirmed in terms of ALD window, saturation and thickness dependence. Lastly, the resulting films were analyzed for their structure, morphology, composition and the optical properties were investigated.

With the successful synthesis and characterization of transition metal β-ketominates, the library of potential precursors for first row transition metals was expanded. As representative examples, the successful development of water assisted ALD processes for iron and zinc oxide is demonstrated. The similarity in the physico-chemical properties of these precursors is an advantage to grow ternary metal oxides.

3:00pm **AF2-MoA-7 A New and Promising ALD Process for Molybdenum Oxide Thin Films: From Process Development to Hydrogen Gas Sensing Applications***, **Jan-Lucas Wree**,* Ruhr University Bochum, Germany*; M Mattinen,* University of Helsinki, Finland*; E Ciftyürek, K Schierbaum,* Heinrich Heine University Düsseldorf, Germany*; M Ritala, M Leskelä,* University of Helsinki, Finland*; A Devi,* Ruhr University Bochum, Germany

The oxides of molybdenum are well known for their versatile properties and therefore serve as excellent materials for a wide range of applications like (photo)catalysis, optoelectronics, and gas sensors for a variety of gas species. Molybdenum oxide can occur in several oxidation states that exhibit very different properties. The different oxides can be distinguished by their crystalline structures as well as by their mechanical and electrical properties. While the different crystalline phases of MoO_3 (α, β, h) are semiconducting with wide band gaps between 2.7 eV and 3.5 eV, the less common suboxides such as Mo_4O_{11} exhibit higher electrical conductivity and the dioxide MoO_2 is even known as pure metallic conductor.[1] Recent studies have shown that α-MoO_3 is a promising material for gas sensing applications owing to its high activity towards gases such as ammonia, nitrogen dioxide and hydrogen at moderate temperatures.[2] Although various oxides of Mo have been tested for the sensing of hydrogen, which is an important source for clean energy, the suboxides of Mo are not well explored for hydrogen sensing.

In this study, we have investigated the feasibility of using the bis(tertbutylimido)bis(N,N'-diisopropyl-acetamidinato) compound of molybdenum $[Mo(N^tBu)_2(dpamd)_2]$ as a potential precursor for atomic layer deposition (ALD) of MoO_x films. In the first part of the study, the focus was to optimize a new ALD process using this precursor together with ozone as the oxygen source. The phase and composition of the layers could be tuned by varying the process parameters which resulted in amorphous (≤250 °C), crystalline suboxide (275 °C), a mixture of suboxide and α-MoO_3 (300 °C), or pure α-MoO_3 (≥325 °C) films. The evaluation of the layers using synchrotron-based surface enhanced photoemission spectroscopy revealed a high amount of oxygen vacancies on the surface of MoO_x suboxide films deposited at 275 °C, which is relevant for sensing applications. Owing to the composition control that could be achieved, the second part of this study focused on evaluating the electrical properties of the MoO_x layers. The temperature dependent resistivity of the MoO_x films suggested them to be suitable for gas sensing applications. In this context, a simple hydrogen gas sensor device was built using 50 nm suboxide MoO_x films which showed reversible and fast response to hydrogen gas at low temperatures.[3] The results derived from this study are very encouraging and form a solid foundation for in-depth studies on tuning the crystallinity of the suboxides for applications beyond gas sensing such as catalysis and energy storage.

3:15pm **AF2-MoA-8 Atomic Layer Deposition of Gallium Oxide Thin Films using Pentamethylcyclopentadienyl Gallium and Combinations of H_2O and O_2 Plasma***, **Fumikazu Mizutani**, S Higashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M Inoue, T Nabatame,* National Institute for Materials Science, Japan

Pentamethylcyclopentadienyl gallium (GaCp*) was synthesized as a new precursor for atomic layer deposition of Ga_2O_3 thin films. GaCp* has higher vapor pressure compared with ethylcyclopentadienyl indium (InEtCp), which we reported previously [1, 2]. GaCp* is a cyclopentadienyl compound having a pentahapto half-sandwich structure as well as the InEtCp. Therefore, Ga_2O_3 thin films could be deposited in a similar way. In this paper, we investigated the role of the combinations of oxidant gases, H_2O followed by O_2 plasma (WpO), H_2O followed by O_2 (WO), and solely O_2 plasma (pO), on deposition mechanism of Ga_2O_3 films by the ALD process with GaCp* precursor.

During WpO process at 200 °C, linear growth with no nucleation delay and with a growth rate (GPC) of approximately 0.06 nm/cycle was observed, when 0.1 s GaCp*, 3 s H_2O, and 50 s O_2 plasma pulse times were applied. For the WpO process, a self-limiting surface reaction occurred when an GaCp* pulse time of 0.1-0.3 s, a H_2O pulse time of 1-5 s and an O_2 plasma pulse time of 40-90 s were applied at 200 °C. At this time, with a short O_2 plasma pulse time of less than 40 s, the oxidation reaction insufficiently carried out and resulted in thinner Ga_2O_3 films.

To understand the role of the surface oxidation step in the ALD process on the GPC, GPCs at 200 °C for WpO process with shorter O_2 plasma pulse time of 14 s (0.1 s GaCp* and 3 s H_2O) and WO process (0.1 s GaCp*, 3 s H_2O, and 50 s O_2) were examined. The GPC for the WO and for the pO process were 0.04 nm/cycle and 0.003 nm/cycle, respectively. If the O_2 plasma pulse time is shortened for WpO process, the GPC becomes slightly smaller. On the other hand, GPC becomes negligibly small without plasma (WO).

Next, the role of the H_2O step on the GPC was investigated. The GPC at 200 °C for pO process (0.1 s GaCp* and 50 s O_2 plasma) was 0.05 nm/cycle, indicating that the oxidation is insufficient compared with WpO process.

The Ga_2O_3 films by plasma-enhanced ALD using a new GaCp* precursor was demonstrated. Based on these experimental data, note that the Ga_2O_3 surface oxidation step is found to be extremely important.

References

[1] F. Mizutani, S. Higashi, and T. Nabatame, AF1-TuM6, 17th International Conference on Atomic Layer Deposition (2017)

[2] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, AF2-TuM15, 18th International Conference on Atomic Layer Deposition (2018)

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