ALD Fundamentals
Room Grand Ballroom A-G - Session AF-MoA
Precursors and Processes

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

4:00pm **AF-MoA-11 Precursors for Photoassisted Area Selective Deposition on Self Assembled Monolayers***, B. Das, R. Singh, C. Brewer,* University of Florida*; R. Holliday, A. Walker,* University of Texas at Dallas*; **Lisa McElwee-White,*** University of Florida **INVITED**

Photoassisted chemical vapor deposition (PACVD), or photochemical CVD, is a technique that can be used for metallization of thermally sensitive substrates such as patterned self-assembled monolayers (SAMs), providing a potential route to area selective deposition (ASD) through different reactivity with the terminal functional groups of the SAM.In this project, photochemical dissociation of the precursor occurs in the gas phase and is dependent upon the photochemical and subsequent thermal reactivity of the precursor.The reactivity is controlled by the excited state properties and bond dissociation energies of the precursor and can be assessed by determining quantum yields for starting material disappearance and appearance of ligand loss products. Screening for the decomposition efficiency of potential precursors for PACVD can be used in a downselection process before deposition experiments begin.

Readily available Ru and Mn compounds, including (η^3-allyl)$Ru(CO)_3X$, (η^4-diene)$Ru(CO)_3$ and $RMn(CO)_5$ complexes, have been assessed for their potential use in ASD by PACVD.Precursor design, electronic structure, and photochemical reactivity of the complexes will be discussed in the context of the results of PACVD of Ru or Mn on functionalized SAMs.

4:30pm **AF-MoA-13 Reductive Thermal ALD of Pd and Au Thin Films***, **Anton Vihervaara**, T. Hatanpää, H. Nieminen, K. Mizohata, M. Chundak, M. Ritala,* University of Helsinki, Finland

Gold and palladium thin films have many potential applications in microelectronics, protective coatings, catalysis and MEMS. Many ALD processes, especially for noble metals, are either highly oxidative or plasma enhanced. While these approaches to the deposition of metal thin films do have their advantages, they also impose challenges. Thus, reductive thermal processes are needed as alternatives. 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine^1 and 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine^2 ($(Me_3Si)_2$DHP and $(Me_3Ge)_2$DHP) are both relatively novel reducing agents with only few reported ALD processes. In our recent research, we developed a low temperature ALD process for nickel using $NiCl_2(PEt_3)_2$ and $(Me_3Ge)_2$DHP.

In this study, ALD of gold^3 and palladium was realized by combining $AuCl(PEt_3)$with $(Me_3Ge)_2$DHP, and $PdCl_2(PEt_3)_2$with $(Me_3Si)_2$DHP. High purity gold films were successfully deposited at 180 °C. Metallic palladium was also deposited at the same temperature. ALD characteristics were confirmed and saturative growth achieved with these processes. While the gold films were extremely pure having less than 0.5 at.% of impurities, Pd films had significantly more of carbon and phosphorus (14 and 5 at.%, respectively). This is likely caused by decomposition of the PEt_3 ligands, catalyzed by the Pd surface. However, since neither film had any chlorine, we can conclude efficient reduction of the metal ions. The resistivities of the films correlated with the impurity contents. The gold films had resistivities very close to the bulk value, while the Pd films had much higher resistivities. The gold process had a growth rate of 1.7 Å/cycle, while for the Pd it was 0.4 Å/cycle. When $PdCl_2(PEt_3)_2$ and $(Me_3Ge)_2$DHP were combined, surprisingly, $PdGe_x$ films were obtained.

Based on these and our earlier experiments, we have successfully extended the combination of volatile metal chloride precursors and DHP-type reducing agents, originally demonstrated with $(Me_3Si)_2$DHP by prof. Winter and co-workers, as an avenue for reductive, oxygen-free thermal ALD of metals. We have also established the applicability of $AuCl(PEt_3)$and $PdCl_2(PEt_3)_2$ in ALD processes, both being valuable additions to the slim library of proper ALD precursors for these metals.

(1) Klesko, J. P. et al. *Chem. Mater.***2015**, *27* (14), 4918–4921. https://doi.org/10.1021/acs.chemmater.5b01707.

(2) Vihervaara, A. et al. *Dalt. Trans.***2022**, *51* (29), 10898–10908. https://doi.org/10.1039/D2DT01347A.

(3) Vihervaara, A. et al. *ACS Mater. Au***2023**. https://doi.org/10.1021/acsmaterialsau.2c00075.

4:45pm **AF-MoA-14 Phosphorus Zintl Species as ALD precursors for Metal Phosphide Thin Films***, **Paul Ragogna**, J. Bentley,* Western University, Canada*; E. Goodwin,* Carleton University, Canada*; J. Lomax,* Western University, Canada*; B. Van Ijzendoorn, M. Mehta,* University of Manchester, UK*; S. Barry,* Carleton University, Canada

Atomic Layer Deposition (ALD) is a thin film deposition technique in which precursors sequentially saturate a substrate surface in a self-limiting reaction. This nanoscale process enables the tuning of instrument parameters to synthesize thin films of controlled thickness which results in varied physical and electronic material properties.[1] Metal phosphide thin films can be prepared by vapour deposition techniques using various combinations of metal and phosphorus precursors, and these materials have applications in microelectronics, catalysis, and energy storage.[2,3] Group 13 and 14 materials such as GaP, InP, and GeP possess bandgaps that are amenable to photovoltaic and transistor applications and are derived from PH_3, an extremely toxic and pyrophoric reagent requiring specialized facilities. [4] Heptaphosphide (P_7^{3-}) is a relatively easy to prepare Zintl species with various binding modes possible with an electron-deficient metal,[5] and given its structural difference from PH_3, a diverse series of metal phosphide film compositions can be produced. In this context, the thermal properties and utility of $P_7(SiMe_3)_3$ as a phosphorus precursor combined with Group 13 species to produce metal phosphide films were investigated. The $P_7(SiMe_3)_3$ cluster is sufficiently robust up to ~250 ºC (by DSC) and the precursor also has virtually no residual mass as measured by TGA, and an extrapolated volatilization temperature at 1 torr (T_v) of ~130 ºC. The volatilization and saturative behaviour of the precursor was analyzed by QCM which demonstrated saturation of an Al_2O_3 crystal to ~16.32 ng/cm^2. As an example of the applicability of $P_7(SiMe_3)_3$, an ALD processes was performed with $P_7(SiMe_3)_3$ and $AlMe_3$ with the investigation of other secondary precursors currently on-going. The resulting materials were investigated using quartz crystal microbalance, XPS, ToF-SIMS, AFM and SEM.

[1]Miikkulainen, V. *et al. J Appl. Phys.* **2013**, 113, 021301; [2] Shi, Y. *et al. Chem. Soc. Rev.*, **2016**, *45*(6), 1529–1541; [3] Callejas, J. F. *et al. Chem. Mat.*, **2016**, *28*(17), 6017–6044;[4] Lu. Y. *et al. RSC Adv.*, **2016**, 6, 87188; [5] Turbervill, R. S. P. *et al. Chem. Rev.*, **2014**, *114*(21), 10807–10828.

5:00pm **AF-MoA-15 Investigation of Discrete Reactant Feeding for Atomic Layer Deposition of In_2O_3 Using Novel Liquid Alkyl-Cyclopentadienyl Indium Precursor***, **Hae Lin Yang**, H. Kim,* Hanyang University, Republic of Korea*; T. ONO, S. KAMIMURA, A. EIZAWA, T. TERAMOTO, C. DUSSARRAT,* Air Liquide Laboratories, Japan*; J. Park,* Hanyang University, Republic of Korea

An interest in indium oxide (In_2O_3)-based metal oxide semiconductors, such as In_2O_3, indium-gallium oxide (IGO), indium-zinc oxide (IZO), and indium-gallium-zinc oxide (IGZO) for the use of electronic devices has been increased. In particular, In_2O_3 is spotlighted as a material capable of controlling oxygen vacancies and impurity concentrations to achieve higher carrier mobility^1. Therefore, an investigation for a novel indium precursor for ALD which is able to obtain a wide process window, superior growth rate, uniformity, and film quality has increased. Nowadays, In_2O_3 film deposition using metal-organic precursors has been fully investigated but the process of high-temperature region, over 300℃, is not much reported due to the thermal stability. Although the precursors that have cyclopentadienyl (Cp) functional groupare reported stably react over 300℃,^{2} InCp is not favorable in the industry because it is a solid phase at room temperature which leads to a particle issue during the process and reported co-oxidant, H_2O and O_2 plasma show poor conformality on the complex structure. For this reason, our group has evaluated the novel indium alkyl cyclopentadienyl, which has high stability, a broad process window (200-400℃), and a liquid phase at room temperature. In this study, not only the introduction of a new precursor but also the development of the deposition process to obtain an order of double higher growth rate than the conventional method. We adopted a discrete reactant feeding (DRF) to improve the growth rate in this study. This optimized ALD process shows a very high growth rate of 2.0Å/cycle and negligibly low residual carbon impurities around the XPS detection limit. Also, a very wide process temperature range (200-400℃) was obtained and various film analysis methods such as XPS, XRR, XRD, and AFM are used to evaluate the In_2O_3 film quality. Therefore, the indium precursor having alkyl cyclopentadienyl derivative is one of the promising candidate precursors to form a high-quality In_2O_3 film for use in the future semiconductor field.

5:15pm **AF-MoA-16 Synthesis and Precursor Property Evaluation of Er Enaminolate Complexes and Deposition of Er_2O_3 Thin Film using Thermal Atomic Layer Deposition (ALD)**, ***Chamod Dharmadasa**, C. Winter, N. Jayakodiarachchi,* Wayne State University*; P. Evans,* University of Wisconsin-Madison*; R. Liu,* University of Wisconsin - Madison

Lanthanide oxide films have many applications in optics, catalysis, and semiconductor devices. Er_2O_3 films have useful properties that arise from its high dielectric constant, a large band gap energy, high refractive index, and thermodynamic stability at high temperatures. These properties have led to the investigation of Er_2O_3 films for possible inclusion in CMOS devices, antireflective and protective coatings on solar cells, and passivation layers for III-V semiconductors. Er_2O_3 films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique since it gives Angstrom-level thickness control and can afford 100% conformal coverage in high aspect ratio features. ALD precursors reported to date for Er_2O_3 films have problems that include low reactivity toward water as a co-reactant, oxidation of substrates when ozone is used as the co-reactant, and variable thermal stabilities. Recently, we described a series of volatile and thermally stable lanthanide(III) complexes that contain enaminolate ligands.[1] We report here detailed synthetic studies of the $Er(L^1)_3$ precursor complex, its ALD precursor properties, and its use in the ALD of Er_2O_3 films using water as the co-reactant. Depending upon the reaction conditions during precursor synthesis the compounds $Er(L^1)_3$, $Er(L^1)_3(L^1H)$, or $K[Er(L^1)_4]$ can be isolated. The reaction conditions can be selected to provide high yields of $Er(L^1)_3$. The volatility and thermal stability characteristics of $Er(L^1)_3$ are favorable for use as precursors for Er_2O_3 and other rare-earth oxides. An ALD window in the growth of Er_2O_3 films using $Er(L^1)_3$ with water as the co-reactant was observed from 150 to 250 °C, with a growth rate of 0.25 Å/cycle. The films were characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy. Advantages of $Er(L^1)_3$ include its simple synthesis, good volatility and high thermal stability, and high reactivity with water to afford Er_2O_3 films. This class of new ALD precursors has the potential to enable more widespread use of the favorable properties of rare-earth oxide compounds and can be expanded to multi-component complex oxides containing rare earths.

1. N. Jayakodiarachchi, P. G. Evans, C. L. Ward, C. H. Winter, *Organometallics***2021**, *40*, 1270-1283.

5:30pm **AF-MoA-17 Deposition of $CsSnI_3$ Perovskite Thin Films by Atomic Layer Deposition and Pulsed Chemical Vapor Deposition**, ***Alexander Weiß**, M. Terletskaia, G. Popov, M. Leskelä, M. Ritala, M. Kemell,* University of Helsinki, Finland

Cesium tin triiodide ($CsSnI_3$) belongs to the group of halide perovskites, materials with outstanding optoelectronic properties. Halide perovskites gained huge interest in the past decade because they can be used as thin film solar absorbers in perovskite solar cells. This young technology has the potential to deliver low-cost solar energy and has already reached promising power conversion efficiencies above 25 %.

$CsSnI_3$ exhibits a small band gap energy (1.2 – 1.3 eV) and is Pb-free, providing a lower toxicity compared to its Pb-containing analogues, such as $CH_3NH_3PbI_3$ (MAPI) or $CsPbI_3$. Therefore, it is an attractive candidate for an environmentally friendlier and less hazardous absorber layer for perovskite solar cells.

Before perovskite solar cells can become widely commercially available, two problems need to be solved: The lacking scalability to large and/or complex-shaped areas, and the instability impeding the durability of the solar cell. We aim to tackle the scalability issue by employing Atomic Layer Deposition (ALD) as the key method. We believe that developing an ALD-based process for $CsSnI_3$ can also address the stability issue of the perovskite layer. Inorganic perovskites, especially solid-solution perovskites, are reportedly more stable than their organic-inorganic hybrid analogues. Combining an ALD-based $CsSnI_3$ process with our earlier $CsPbI_3$ ALD process[1] or our ALD-based MAPI process[2] would enable the scalable deposition of such solid-solution halide perovskites.

In this work, we report two new ALD-based routes to deposit $CsSnI_3$ thin films. The first route relies on a two-step approach, starting with the deposition of ALD CsI[1] that is subsequently exposed to a new ALD SnI_2 process to convert it to $CsSnI_3$. The ALD SnI_2 process uses $Sn(btsa)_2$ (btsa: bis(trimethylsilyl)amide) and SnI_4 as precursors, works in a narrow temperature range (75 – 90 °C) on CsI and yields phase-pure γ-$CsSnI_3$ films. The second route relies also on the deposition of ALD CsI but in this case it is converted to γ-$CsSnI_3$ by pulsed Chemical Vapor Deposition (pCVD) of SnI_2 using the same precursors. This process works at similar temperatures (160 – 180 °C) as the ALD CsI process, therefore effectively making it a one-step approach that is much faster than the first route. Moreover, exposing the CsI film to the pCVD SnI_2 process at these elevated temperatures ensures that the excess SnI_2 is sublimed, making this process self-limiting with respect of the ternary film composition.

[1] A. Weiß et al., *Chem. Mater.* **2022**, 34, 13, 6087–6097

[2] G. Popov et al., *Chem. Mater.* **2019**, 31, 3, 1101–1109

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