ALD Fundamentals
Room Grand Ballroom H-K - Session AF2-TuM
ALD Precursors II

Moderators: Jin-Seong Park, Hanyang University, Seán Barry, Carleton University

8:00am **AF2-TuM-1 Characterizing Water Delivery for ALD Processes**, ***James Maslar**, B Sperling, W Kimes,* National Institute of Standards and Technology*; W Kimmerle, K Kimmerle,* NSI*; E Woelk,* CeeVeeTech

Water is utilized as the oxygen source for many metal oxide ALD processes. Water is commonly delivered in an inert carrier gas from a bubbler (an ampoule with a dip tube) or a vapor draw ampoule (an ampoule with no dip tube: the gas in and gas out ports open directly into the ampoule headspace). While it is relatively simple to implement a delivery system based on such ampoules, it can be difficult to reproducibly deliver water from such ampoules. This is at least in part due to evaporative cooling, i.e., cooling reduces the water vapor pressure and hence the amount of material entrained in the carrier gas. For an ideal ALD process, irreproducible water delivery may not lead to undesirable changes in the deposited film properties (unless the dose is insufficient to saturate the reactive surface sites). However, if the ALD process involves a chemical vapor deposition component, irreproducible water delivery can result in undesired film properties. The goal of this work is to obtain a better understanding of the factors influencing water delivery from bubblers and vapor draw ampoules. To achieve this goal, both the amount of water delivered from an ampoule and the temperature distribution of the water in the ampoule were measured under a range of process conditions, in bubblers and vapor draw ampoules. The amount of water delivered and the water temperature vertical distribution in the ampoule were measured using a tunable diode laser spectroscopy system and a five-element temperature sensor array, respectively. These data were used determine the degree to which the amount of water delivered was correlated to evaporative cooling in the ampoule. For bubblers, this determination was relatively straight-forward as bubbling tended to homogenize the water temperature. For vapor draw ampoules, however, this determination was complicated by a temperature gradient that existed during flow. The focus of this investigation was on commercial 1.5 L ampoules (with a maximum fill of 1.2 L), although different ampoule designs were examined. The results from this work could facilitate development of ALD process recipes, delivery control methods, and improved ampoule designs.

8:15am **AF2-TuM-2 A Nickel Chloride Adduct Complex as a Precursor for Low-Resistivity Nickel Nitride Thin Films with Tert-butylhydrazine as a Coreactant**, *K Väyrynen, T Hatanpää, M Mattinen, M Heikkilä, K Mizohata, J Räisänen,* University of Helsinki, Finland*; J Link, R Stern,* National Institute of Chemical Physics and Biophysics, Estonia*; M Leskelä, **Mikko Ritala**,* University of Helsinki, Finland

From the very beginning of ALD, metal chlorides have been extensively used precursors because of their high thermal stability and reactivity as well as low cost. However, not all metal chlorides are volatile enough to be used in ALD. Cobalt and nickel chlorides for example have a polymeric structure and therefore low volatility. To circumvent this limitation, we have recently explored a strategy of adducting these chlorides with chelating ligands. With properly selected diamines the adduct complexes are monomeric and thermally stable enough to be volatilized and used in ALD. These compounds have been earlier been used for deposition of CoO [1] and intermetallics Co_3Sn_2 and Ni_3Sn_2 as a novel class of ALD materials [2].

Herein, we have studied ALD of nickel nitride and nickel thin films using $NiCl_2$(TMPDA) (TMPDA = *N,N,N′,N′,*-tetramethyl-1,3-propanediamine) as the metal precursor and tert-butylhydrazine (TBH) as a nitrogen containing reducing agent. The films were grown at low temperatures of 190–250 °C. This is one of the few low-temperature ALD processes that can be used to grow Ni_3N and Ni metal on both insulating and conductive substrates. X-ray diffraction showed reflections compatible with either hexagonal Ni or Ni_3N. ToF-ERDA analyses showed that the films were close to stoichiometric Ni_3N. Upon annealing the films at 150 °C in 10% forming gas their nitrogen content lowered down to 1.2 at.%, and the nonmagnetic nitride films were converted to ferromagnetic Ni metal.

[1] K. Väyrynen, K. Mizohata, J. Räisänen, D. Peeters, A. Devi, M. Ritala, M. Leskelä, *Chem. Mater.***2017**, *29*, 6502.

[2] K. Väyrynen, T. Hatanpää, M. Mattinen, K. Mizohata, K. Meinander, J. Räisänen, J. Link, R. Stern, M. Ritala, M. Leskelä, *Adv. Mater. Interfaces***2018**, *12*, 1801291.

8:30am **AF2-TuM-3 Simple, Rationally Designed Aluminum Precursors for the Deposition of Low-impurity AlN Films**, ***Sydney Buttera**, S Barry,* Carleton University, Canada*; H Pedersen,* Linköping University, Sweden

Main group chemistry has been integral in the field of ALD since its inception, particularly concerning the extensive work on the most fundamental ALD process: the deposition of aluminum oxide from trimethylaluminum (TMA) and water. It is surprising that strategically functionalized analogues to this fundamental precursor have not been more extensively studied in order to optimize subsequent deposition processes. A simple, rationally designed precursor can regulate surface chemistry and limit decomposition pathways, permitting straightforward reactivity. Our focus is to enable the deposition of low-impurity aluminum nitride by ALD.

This presentation will describe the study of a set of simple molecules that are novel as ALD precursors, based on a substituted TMA framework (Figure 1a-c). Tris(dimethylamido)aluminum(III) is a direct analogue of TMA with methyl groups replaced by dimethylamido ligands. It demonstrates excellent ALD precursor behaviour with a 1 Torr temperature of 67 °C and no decomposition visible by TGA, likely attributed to the stabilization of the Al centre by the coordinative donation from the bridging NMe_2. This precursor deposited aluminum oxide and aluminum oxy-nitride films with carbon impurities lower than those reported using TMA.[1] From this, it was deduced that metal-nitrogen bonds in precursor design were beneficial to stabilizing the metal centre, and importantly, in lowering carbon contamination in deposited films by eliminating direct Al-C bonds.

Using the same TMA framework, $AlH_x(NMe_2)_{3-x}$ (x = 1, 2) compounds were prepared due to the potential for the reducing ability of the hydride ligand and a maintained absence of metal-carbon bonds. These compounds were also found to be volatile and thermally stable, and thus suitable as potential AlN precursors.

This led to the study of further nitrogen-containing ligands: the family $Al(^{Me}NacNac)_x(NMe_2)_{3-x}$ (x = 1, 3) similarly showed excellent volatility and thermal stability. Interestingly, an Al species with one monoanionic and one doubly anionic ^{Me}NacNac ligand was discovered (Figure 1d) and presented this novel reduced ligand for potential use in ALD precursors. This compound was synthesized via reduction of the ^{Me}NacNac ligand, and its thermal characterization and reactivity, as well as that of contrarily unsuitable ALD candidates using these ligands, will also be discussed in this presentation.

[1] Buttera, S. C.; Mandia, D. J.; Barry, S. T. Tris(dimethylamido)aluminum(III): An Overlooked Atomic Layer Deposition Precursor. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.***2017**, *35* (35), 1–128.

8:45am **AF2-TuM-4 Atomic Layer Deposition of Lead(II) Sulfide at Temperatures Below 100 °C**, ***Georgi Popov**,* University of Helsinki, Finland*; G Bačić,* Carleton University, Canada*; M Mattinen, M Vehkamäki, K Mizohata, M Kemell,* University of Helsinki, Finland*; S Barry,* Carleton University, Canada*; J Räisänen, M Leskelä, M Ritala,* University of Helsinki, Finland

Lead(II) sulfide (PbS) is one of the oldest known semiconductors. It has a narrow band-gap of 0.4 eV that can be widened by quantum confinement effects. Owing to these properties, PbS is a recognized material in IR detection and quantum dot (QD) based devices such as light emitting diodes (LEDs) and photovoltaics. Photovoltaics are also central to our study. The aim is to develop an ALD PbS process that can be applied in halide perovskite solar cells.

ALD processes for PbS exist at least since 1990[1], however we discovered that known ALD PbS processes are incompatible with halide perovskites such as $CH_3NH_3PbI_3$ due to their extremely low thermal budget[2]. To our knowledge the lowest temperature at which PbS can be deposited with existing ALD processes is 130 °C.[3] $CH_3NH_3PbI_3$ film degrades completely at that temperature in our ALD reactors. Thus, we set out for a new PbS process that would work at even lower temperatures. From our previous studies on ALD of PbI_2 we already knew one lead precursor suitable for low temperature ALD: lead(II) bis[bis(trimethylsilyl)amide] or $Pb(btsa)_2$.[4] Recently Bačić et al. reported another suitable candidate: lead(II) *rac*-N^2,N^3-di-*tert*-butylbutane-2,3-diamide or Pb(dbda).[5] With these lead precursors and H_2S as a co-reactant we developed two new processes capable of depositing PbS even below 100 °C.

$Pb(btsa)_2$-H_2S process produces uniform, high-quality, crystalline PbS films in the 65 – 155 °C range. TOF-ERDA composition analysis revealed exceptionally high purity for such low deposition temperatures. The process exhibits two regions with temperature independent growth per cycle values (GPC) of 0.50 Å and 0.15 Å at 65 – 80 °C and 115 – 155 °C, respectively. The GPC saturates rapidly with respect to both precursor pulses and is independent of the purge duration and number of deposition cycles. $CH_3NH_3PbI_3$ films survive the PbS deposition at the lowest deposition temperatures and studies of perovskite stability after PbS deposition are ongoing.

With Pb(dbda) film deposition occurs in an even wider temperature range of 45 – 155 °C. However, XRD measurements show that at 95 °C and above, the films contain crystalline impurities. Nevertheless, high-quality polycrystalline PbS films can be deposited at temperatures as low as 45 – 75 °C. We are currently conducting studies on the influence of process parameters on the PbS film properties.

[1] Leskelä et al. *Vac.* **1990**, 41, 1457–1459.

[2] Zardetto et al. *Sustain. Energ. Fuels* **2017**, 1, 30-55

[3] Nykänen et al. *J. Mater. Chem.* **1994**, 4, 1409.

[4] Popov et al. *Chem. Mater.* **2019,** Article ASAP. DOI: 10.1021/acs.chemmater.8b04969

[5] Bačić et al. *Inorg. Chem.* **2018**, *57*, 8218-8226.

9:00am **AF2-TuM-5 Development and Characterization of a Novel Atomic Layer Deposition Process for Transparent p-Type Semiconducting Nickel Oxide using Ni(^{tBu2}DAD)$_2$ and Ozone***, Konner Holden,* Oregon State University*; C Dezelah,* EMD Performance Materials*; J Conley, Jr.,* Oregon State University

Nickel oxide (NiO), a wide band gap p-type oxide semiconductor, is of interest for applications in solar energy conversion,[1] electrocatalysis,[2] and as a tunnel barrier for metal/insulator/metal (MIM) diodes for infrared energy harvesting.[3] ALD is an ideal technique for the highly conformal, uniform thin films needed for these applications. We develop a new process for ALD of NiO using Ni(^{tBu2}DAD)$_2$ and O_3-.

ALD growth of metallic Ni was demonstrated recently using Ni(^{tBu2}DAD)$_2$ and *tert*-butylamine.[4] ALD of metallic Co and cobalt oxide have been reported using Co(^{tBu2}DAD)$_2$ with formic acid and O_3, respectively.[5,6] Taking a similar approach, we deposit NiO in a Picosun Sunale R-150 using N_2-purge-separated cycles of Ni(^{tBu2}DAD)$_2$ held at 150°C and an O_3/O_2 mixture of ~10%. NiO films were characterized using grazing-incidence x-ray diffraction (GIXRD), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), variable angle spectroscopic ellipsometry (VASE), and p-NiO/n-Si heterojunction diodes.

A plot of GPC vs. temperature for depositions using a 5/30/4/30 s Ni(^{tBu2}DAD)$_2$/N_2/O_3/N_2 pulse sequence shows a clear ALD "window" of constant GPC = 0.12 nm/cycle from 185-200 °C (Fig. 1) in which Ni(^{tBu2}DAD)$_2$ and O_3 pulses saturate after ~5 s and ~4 s, respectively (Fig. 2). Below the temperature window, condensation of Ni(^{tBu2}DAD)$_2$ occurs resulting in uncontrolled growth with 1.2% C and 0.7 % N impurities (XPS) at 150 °C. Above the window, from 200-230 °C, desorption of Ni(^{tBu2}DAD)$_2$ occurs, followed by decomposition of Ni(^{tBu2}DAD)$_2$ above 230 °C on the chamber walls upstream of the wafer, both contributing to decreased GPC. Inside the temperature window, for saturating films deposited at 200 °C, GIXRD shows randomly-oriented polycrystalline cubic NiO (Fig. 3), consistent with XPS elemental analysis showing a Ni:O ratio near unity, without any detectable C or N impurities. VASE reveals that refractive index (~2.4) and band-gap (~3.8 eV) are close to bulk values while AFM RMS roughness was 0.6 nm for an 18 nm thick film (Fig. 4). p-NiO/n-Si diodes show highly asymmetric ($I_+/I_{-,MAX} \approx 10^4$) behavior. All results point towards an as-deposited transparent p-type semiconducting NiO. Further growth studies, characterization, and electrical measurements will be discussed at the meeting.

1. S. Seo et al., Nanoscale 8, 11403 (2016).
2. K. L. Nardi et al., Adv. Energy Mater. 5 (2015).
3. N. Alimardani et al. Appl. Phys. Lett. 105, 082902 (2014).
4. M. M. Kerrigan et al., ACS Appl. Mat. & Interfaces. 10, 14200 (2018).
5. J. P. Klesko, M. M. Kerrigan, and C. H. Winter, Chem. Mater. 28, 700 (2016).
6. J. Kim et al., Chem. Mater. 29, 5796 (2017).

9:15am **AF2-TuM-6 Blocking Thermolysis in Diamido Plumbylenes***, **Goran Bacic**,* Carleton University, Canada*; D Zanders,* Ruhr University Bochum, Germany*; I Frankel,* Carleton University, Canada*; J Masuda,* Saint Mary's University, Canada*; T Zeng,* Carleton University, Canada*; B Mallick, A Devi,* Ruhr University Bochum, Germany*; S Barry,* Carleton University, Canada

Lead-containing nanomaterials like PbS quantum dots and $CH_3NH_3PbI_3$ perovskite films have received a frenzy of attention because of their unique optoelectronic properties. Atomic layer deposition (ALD) is an especially attractive method for their fabrication as it can deposit uniform, conformal films over large areas at low temperatures with subnanometer thickness control. However, current lead-containing ALD processes have rarely been adopted due to their poor thermal budget, the low volatility of known precursors, and the small library of thermally robust lead complexes. Our interest in the deposition of lead-containing materials prompted us to study amido ligands because of their low cost, flexibility, and proven effectiveness of other group 14 diamido complexes as precursors for ALD.

In a pilot study,[1] we identified the thermally stable (dec. >100 °C) and highly volatile (subl. 40 °C/0.01 Torr) 5-membered *N*-heterocyclic plumbylene *rac*-N^2,N^3-di-*tert*-butylbutane-2,3-diamido lead(II) (**1**), however it failed to cleanly react with our sulfur-source *tert*-butylthiol below its decomposition temperature. To explore safe (i.e., less reactive) co-reagents for ALD, we needed to push the thermal stability even higher through a mechanistic understanding of the decomposition pathways of diamido plumbylenes. With few reports on the mechanisms of their thermolysis, we decided to undertake a combined synthetic and theoretical approach to this problem. The two most promising examples in the literature, **1** and Pb[N(SiMe$_3$)$_2$], suggested both cyclic and acyclic scaffolds were viable.

We postulated two dominant thermolysis pathways for plumbylenes: formation of metallacycles by π-overlap of *N*-substituents and the 6p^0 orbital of lead (**A**); and concerted pericyclic cycloreversion reactions (**B**). We found experimentally that known acyclic complexes were dominated by **A,** and 5-membered cyclic derivatives were found to be dominated by pathway **B** so we designed bespoke ligands to block thermolysis through two strategies: coordinatively saturating lead with a Lewis base to hinder **A**, and rigid ligands to block **B**. *Ab initio* calculations were performed on a model set of plumbylenes to help reveal the way forward to indefinitely robust and volatile plumbylenes for deposition, and provide a better understanding of the unique ligand-metal cooperation required for lead.

[1] Bačić, G., Zanders, D., Mallick, Devi, A., Barry, S.T.Designing Stability into Thermally Reactive Plumbylenes. *Inorg. Chem.***2018**, *57* (14), pp 8218-8226.

9:30am **AF2-TuM-7 ALD of Sc_2O_3 with Sc(cp)$_3$ and a Novel Heteroleptic Precursors***, T Ivanova, **Perttu Sippola**,* ASM, Finland*; G Verni, Q Xie,* ASM, Belgium*; M Givens,* ASM, Finland

The deposition and the properties of rare earth oxide thin films have been extensively studied for applications as protective coatings, optics and microelectronics. Sc_2O_3 thin films have recently attracted a strong interest for application as gate dielectrics for metal-oxide-semiconductor field-effect transistors (MOSFET) because they have a dielectric constant of 14, a band gap of 6.3 eV and excellent thermal stability. Despite its advantages, very few studies have investigated Sc_2O_3 on Si. We therefore investigated growth characteristics of Sc_2O_3 films deposited by atomic layer deposition (ALD) from Sc(cp)$_3$ and a novel liquid heteroleptic cyclopentadienyl containing Sc precursor, which are thermally stable (>300 ˚C), volatile, with a good reactivity to H_2O. The depositions were done in a hot-wall cross-flow-type ASM Pulsar® 3000 reactor connected to a Polygon 8300 platform.

The film growth properties, such as growth per cycle, impurity concentrations, and thickness uniformity on 300 mm Si (100) wafers were studied. A growth rate per cycle of 0.46 Å/ cycles and 0.52 Å/cycle was obtained at 225 ˚C with novel Sc based precursor and Sc(cp)$_3$, respectively. The Sc_2O_3 film non-uniformity was about 1 % and 5 % with novel Sc heteroleptic precursor and Sc(cp)$_3$, respectively. Sc_2O_3 films based on the novel Sc precursor were stoichiometric, with a low C impurity content of <1%, while films based on Sc(cp)$_3$ precursor exhibited ~4.5 % of residual carbon impurity level under similar processing conditions.

Electrical measurements were done on planar TiN gated MOS capacitor (MOSCAP) with high k thickness ~8 nm. Sc(cp)$_3$ based Sc_2O_3 exhibited a leakage current density of 1.5 x 10^{-4} A/cm^2 and an effective work function (eWF) of 4.05 eV for an equivalent oxide thickness (EOT) of 3.43 nm at 1.0 V, which is significantly lower than TiN eWF (~4.8 eV) indicating considerable positive fixed charges incorporated in deposited Sc_2O_3 film. While novel heteroleptic Sc based Sc_2O_3 films exhibited much lower leakage current density of 1.0 x 10^{-8} A/cm^2 and close to TiN eWF of 4.77 eV for an EOT of 3.15 nm at 1.0 V. It was shown that good quality and low defects Sc_2O_3 films can be obtained by using the novel heteroleptic Sc precursor.

9:45am **AF2-TuM-8 A Novel Self-limited Atomic Layer Deposition of WS_2 based on the Chemisorption and Reduction of bis(t-butylimido)bis(dimethylamino) Complexes***, Nicola Pinna,* Humboldt-Universtät zu Berlin, Germany

A novel self-terminating chemical approach for the deposition of WS_2 by atomic layer deposition based on chemisorption of bis(t-butylimido)bis(dimethylamino)tungsten(VI) followed by sulfurization by H_2S is reported. A broad spectrum of reaction parameters including temperatures of the reaction chamber and the precursor and durations of every ALD step are investigated and optimized to reach a high growth per cycle of 1.7 Å and a high quality of the deposited thin films. The self-terminating behaviour of this reaction is determined by the variation of the dose of the precursors. The physical, chemical and morphological properties are characterized by a combination of analytical techniques. XRD, XPS and Raman prove that highly pure and well-defined WS_2 layers can be synthesized by ALD. TEM and AFM images show that WS_2 grows as platelets with a thickness of 6^{-10} nm and diameter of 30 nm, which do not vary dramatically with the number of ALD cycles. A low deposition temperature process followed by a post annealing under H_2S is also investigated in order to produce a conformal WS_2 film. Finally, a reaction mechanism could be proposed by studying the chemisorption of bis(t-butylimido)bis(dimethylamino)tungsten(VI) onto silica, and the thermal and chemical reactivity of chemisorbed species by ^{1}H NMR, GC-MS and FT-IR.

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