ALD Fundamentals
Room Hall 3A - Session AF1-TuA

Precursors and Chemistry: Precursor Design, New Precursors, Process Development III

Moderators: Anjana Devi, Ruhr University Bochum, **Paul Williams**, Pegasus Chemicals

1:30pm **AF1-TuA-1 New Class of Tin Precursors Targeting Low Temperature ALD Processing***, **Jean-Pierre Glauber**, A. Devi,* Ruhr University Bochum, Germany

Motivated by the ever-increasing interest for low temperature atomic layer deposition (ALD) processes of tin-based nanomaterials to implement them in flexible devices or sensitive material stacks, new precursors with prerequisites for ALD are of key interest. Although several tin precursors have been reported, low temperature processing require a distinct reactivity to ensure a clean ligand cleavage at the targeted moderate process conditions.[1-4]

All-nitrogen coordinated chelating ligands with several metals have garnered increasing scientific attention while they impart reactivity and suitable thermal stability because of the chelating effect. Among them, amidinate based complexes such as tin(II)amidinates and tin(II)formamidinates have been in the focus, but their strong binding nature can lead to insufficient ligand cleavage leading to impurities in the thin films.[1-4] This can be attributed to their delocalized electron ligand-metal system that significantly increases their stability, but could make complete ligand cleavage difficult, especially when moderate process conditions are targeted.

To tackle this issue, alternative chelating ligand systems such as geminal diaminosilane (gDAS) are promising alternatives as demonstrated for several metals including Co, V, Ni and Mg.[1,5] In this study, a systematic variation of the gDAS ligand side chains resulted in tin compounds [Sn(*t*Bu–gDAS)$_2$] (**1**) and [Sn(gDAS)$_2$] (**2**) which were characterized thoroughly by complementary analytical methods including NMR, FTIR, EA, SCXRD, EI-MS and LIFDI-MS. The monomeric nature of the complexes was confirmed by LIFDI-MS measurements and SCXRD. Thermal analysis and vapor pressure determination revealed favorable volatility. This study reveals, that the distinct changes in the ligand side chain can have significant influence on their respective thermal behavior. The encouraging thermal properties of the complexes makes them appealing for application in low temperature ALD processes of tin-based nanomaterials which is exemplified with ALD of SnO_x.

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1:45pm **AF1-TuA-2 Novel Synthesis Route for Atomic Layer Epitaxy of $BaSnO_3$***, **Andreas Alstad**, H. Sønsteby,* University of Oslo, Norway

Since 1965 Moore's law has predicted the development of transistor density for decades, but silicon-based devices are reaching their physical limits. Even HfO_2, a high-κ dielectric which replaced the SiO_2 gate oxide in 2007, will soon meet the same fate. New materials are thus needed to further evolve electronic devices with regards to performance and industrial feasibility. An emerging class of materials that may bring about a new paradigm of device design are complex oxides. Their cations can easily be substituted via doping to alter and tune their electronic properties. The research on these materials in the context of microelectronics has barely scratched the surface, as there are numerous atomic configurations of ternary oxides yet to be explored. If one considers quaternary oxides and beyond, then the possibilities border on countless. Nanoscale electronic devices are extremely sensitive to impurities and defects, which is why atomic layer deposition (ALD) is increasingly being used in manufacturing to ensure uniformity and conformality. One promising candidate in this paradigm shift is the perovskite $BaSnO_3$ (BSO). BSO is a transparent wide-bandgap n-type semiconductor that has gotten attention for its excellent charge carrier mobility, especially when doped with lanthanum, making it a promising candidate for high-frequency electronics and other applications where good charge carrier transport is important. It also shows excellent thermal stability.

Designing an ALD process for BSO and characterizing it is the topic of this work. The ALD processes for SnO_2 and BaO have been optimized separately both at a deposition temperature of 300 °C. X-ray fluorescence spectroscopy of our SnO_2 films using $Sn(IV)Cl_2(acac)_2$ found no chlorine impurities in the film. Additionally, we have demonstrated gas sensing capabilities of our SnO_2 thin films. The deposited barium films using $Ba(^iPr_3Cp)_2$ contain both $BaCO_3$ and BaO, confirmed by Fourier-transform IR spectroscopy. The next step is to tune the stoichiometry of the ternary ALD process. Combining these into BSO thin films likely requires post-deposition annealing to decompose and remove the carbonate. The last deposition will attempt epitaxial growth of BSO on a $SrTiO_3$ substrate. Finally, we will investigate the electronic properties of BSO as function of its thickness, such as charge carrier mobility.

$BaSnO_3$ sees potential uses in microelectronics as a transistor channel material for its mobility, but also in photovoltaics as an electron transport layer (ETL) to reduce the probability of electron-hole recombination, and as a transparent conducting oxide (TCO) for displays and touch screens.

2:00pm **AF1-TuA-3 Microwave Enhanced ALD of Al_2O_3***, B. Kupp, A. Schraner, **John Conley**,* Oregon State University

While advantageous for many applications, the low deposition temperature characteristic of ALD can allow incorporation of -OH groups or residual impurities from unreacted ligands leading to non-ideal stoichiometry and sub-optimal physical, optical, and electrical properties. Although increasing deposition temperature and post deposition annealing can help drive off impurities, increase density, improve stoichiometry, adjust morphology, and improve properties of ALD films, these strategies can move a process out of the ALD regime or exceed the thermal budget of sensitive substrates or devices, respectively. To maintain the low thermal budget of ALD while maximizing film properties, annealing or adding energy *during* each (or every few) ALD cycle or supercycle can help drive/speed reactions and reduce impurity/ligand incorporation. Energy enhanced (EE)-ALD methods to date include in-situ rapid thermal (MTA, DADA, etc.) annealing, flash lamp, plasma exposure, and UV, and electric field [1-15].

Here, we introduce microwave enhanced (MWE) ALD using an MKS SG 1024 solid state microwave (MW) generator with a custom antenna integrated into a Picosun R200 PEALD. Al_2O_3 films were deposited at 300 °C using TMA and H_2O. Thickness was measured using a Film Sense FS-1 mapping ellipsometer. Adding a 30 s in-situ 400 W MW exposure (without plasma generation) during the TMA purge part of each ALD cycle reduced film thickness by ~2% across a 150 mm Si wafer (Fig. 1). Preliminary leakage measurements on MOS devices suggest an associated reduction in low field leakage (1 MV/cm) and decrease in the onset-voltage for Fowler-Nordheim conduction. Additional results to be presented include placement of MW exposure step within ALD cycle, temperature, electrical data, morphology, and other materials. MWE-ALD merits further investigation as an EE-ALD technique.

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2:15pm **AF1-TuA-4 Atomic Layer Deposition of SnO Film Using Liquid $Sn(EtCp)_2$ Precursor and Combinations of H_2O and H_2 Plasma***, **Fumikazu Mizutani**, N. Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; T. Nabatame,* National Institute for Materials Science, Japan

The SnO_2 (Sn^{4+}) and SnO (Sn^{2+}) films have been widely investigated as n-type and p-type oxide semiconductors, respectively, for oxide TFTs. We previously reported characteristics of SnO_2 films deposited by ALD using a new Sn precursor (bis(ethylcyclopentadienyl) tin; $Sn(EtCp)_2$) and O_2 plasma [1]. In this study we investigated SnO films formation by ALD with the same

$Sn(EtCp)_2$ and combination of a weak oxidant H_2O and a strong reduction H_2 plasma gases.

At first, the usefulness of H_2O gas on formation of the SnO film during ALD with $Sn(EtCp)_2$ was studied. The growth temperature was 200 °C and ALD cycle was 100. Surprisingly, no growth of SnO film was observed because the thickness of the SnO film was less than 1 nm regardless of the number of ALD cycle. This was quite different results from our previous research of ALD of ZnO using a similar two-coordinated cyclopentadienyl complex and H_2O [2]. This was thought to be due to insufficient adsorption of $Sn(EtCp)_2$ on the SnO surface.

To solve this problem, we investigated ABC type ALD in which H_2 plasma treatment is applied to the SnO surface so that $Sn(EtCp)_2$ is well adsorbed. ALD process was conducted by using $Sn(EtCp)_2$ as a precursor and H_2O followed by H_2 plasma as co-reactants. SnO films were deposited on 150 mm Si wafers with native oxide films at a growth temperature of 200 °C. Saturation of reaction was confirmed when 0.2 s of $Sn(EtCp)_2$, 3 s of H_2O, and 5 s of H_2 plasma pulse times were applied. At this condition, linear growth of SnO film was observed, and the growth per cycle (GPC) was approximately 0.05 nm/cycle. This GPC is relatively high compared to the previously reported values for ALD of SnO [3]. Note that the high GPC shown in Ref. [3] is the value under low growth temperature conditions, and the GPC at a growth temperature of 200 °C is quite low at about 0.01 nm/cycle.

SnO thin films were deposited by ALD using a new cyclopentadienyl-based precursor and combinations of H_2O and H_2 plasma. Linear growth with high GPC of SnO thin film was confirmed.

Reference
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2:30pm **AF1-TuA-5 A New Water Assisted ALD Process for Sc_2O_3 Using a Volatile Liquid Precursor***, **Martin Wilken**,* Ruhr Universität Bochum, Germany*; T. Hepp, O. Briel,* Dockweiler Chemicals GmbH, Germany*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; C. Cho,* Ruhr Universität Bochum, Germany*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; A. Devi,* Leibniz Institute for Solid State and Materials Research, Dresden (IFW), Germany

Scandium oxide (Sc_2O_3) thin films have garnered significant attention in recent years due to their unique properties and versatile applications. The unique combination of high melting point, wide bandgap, high refractive index, and excellent dielectric properties makes scandium oxide an attractive candidate for advanced electronic and optoelectronic devices, such as memory devices, and photodetectors.[1] In particular, the ability of scandium oxide to serve as a high-k dielectric material in thin film transistors (TFT's)[2], highlights the need for versatile low temperature atomic layer deposition (ALD) processes. Although ALD is beneficial to form highly uniform, pure and homogeneous layers of Sc_2O_3 on nanostructured surfaces, there are very few Sc precursors that include the tris-cyclopentadienyl scandium ($[ScCp_3]$)[3], substituted tris–R-cyclopentadienyl scandium ($[Sc(RCp)_3]$(R=Me,Et,^{i}Pr))[4] and scandium betadiketonates ($[Sc(thd)_3]$)[5]. These compounds are associated with certain drawbacks such as low vapor pressure, short shelf life, limited thermal stability and low reactivity. The homoleptic scandium amidinates such as scandium tris-(N,N´-diisopropylacetamidinate)[6] have limited volatility as well.

In our study, we targeted the commercially available new liquid scandium precursor ASGARD [$(EtCp_2Sc(dbt)$] (dbt=1,3-bis(1,1-dimethylethyl)-1-triazenato) (Figure 1). Following up on a thorough investigation of the spectroscopical, structural and thermal properties, we adopted a computational approach to evaluate its use in ALD applications. Structure and ligand dissociation energies were calculated and gave a first indication for its suitability as ALD precursor. Furthermore, the interaction towards oxygen and water was investigated, showing its high degree of reactivity. Finally, the promising attributes of this precursor were proven by the development of a water-based ALD process in the temperature range between 220°C and 275°C. Apart from the ALD characteristics like linearity and saturated growth, the high purity of the Sc_2O_3 films could be proven by compositional analysis employing RBS/NRA (Figure 1). These results unveil the favorable characteristics of the new Sc precursor for Sc_2O_3 thin film growth.

2:45pm **AF1-TuA-6 Atomic Layer Deposition of Crystalline Molybdenum Trioxide and Suboxide Thin Films***, **Alexey Ganzhinov**, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Molybdenum oxides (MoO_x) have a range of different oxidation states and crystal structures which affect material properties significantly, leading to a wide range of applications. In addition to the most common stoichiometric molybdenum oxides, such as dioxide (MoO_2) and trioxide (MoO_3), there are multiple nonstoichiometric MoO_x suboxides where x is between 2.75 and 3. Additionally, molybdenum oxides can change oxidation states relatively easily between Mo^{4+}, Mo^{5+}, and Mo^{6+}. This wide range of possible oxidation states and structures allows the control of optical, electrical, and catalytic properties of the material. For example, the resistivity of molybdenum oxide changes from almost metallic for MoO_2 and Mo_4O_{11}, to semiconducting Mo_9O_{26}, and insulating MoO_3. Emerging applications of MoO_x thin films are (organic) semiconductors, organic and perovskite solar cells, catalytic surfaces, and gas sensors.

Due to the plethora of possible different oxides with varying material properties, many new atomic layer deposition (ALD) processes are needed to cover them all. We developed a new ALD process for crystalline MoO_x thin films and deposited first crystalline ALD MoO_x thin films at 200 °C. Molybdenum acetate dimer ($Mo_2(OAc)_4$) and ozone (O_3) were used as precursors at 200 --– 300 °C in a flow type F120 ALD reactor. Films deposited at low temperatures consist purely of unidentified suboxide phase while higher temperatures show α-MoO_3 phase in the GIXRD measurements. The growth rate of the process ranges from ~0.4 Å/cycle at low temperatures to ~3 Å/cycle at 300 °C.

In-depth composition characterization of the films will be made with X-ray photoelectron spectroscopy (XPS) and time-of-flight elastic recoil detection analysis (TOF-ERDA). Further deposition parameters, such as oxidant type and dose, will be investigated to tune the oxidation state of the thin films from suboxide to trioxide and vice versa during the deposition. Lastly, optical differences between the oxides will be investigated with UV-VIS spectroscopy.

3:00pm **AF1-TuA-7 Promising Precursor Chemistry for ALD of Lithium-Based Thin Films***, **Jorit Obenlüneschloß**,* Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany*; N. Boysen,* Fraunhofer Institute for Microelectronic Circuits and Systems, Duisburg, Germany*; U. Brokmann,* Inorganic Non-metallic Materials, Technische Universität Ilmenau, Ilmenau, Germany*; D. Rogalla,* RUBION, Ruhr University Bochum, Bochum, Germany*; E. Rädlein,* Inorganic Non-metallic Materials, Technische Universität Ilmenau, Ilmenau, Germany*; A. Devi,* Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany

Lithium-containing materials have been particularly difficult to be realized by ALD. This has been mostly attributed to the unavailability of suitable precursor chemistry.[1] That is in stark contrast to the desire to incorporate lithium-containing thin films for battery applications on the large scale.[2] Efforts to utilize oxygen-based precursors such as diketonates (THDs) with low volatility or alkoxides with low thermal stabilities and reactivities are not really promising. Progress has been made with the trimeric lithium hexamethyldisilazane $[Li(HMDS)]_3$ in the past as a more reactive precursor, but this trimeric compound only provides mild reactivities compared to unstable but highly reactive monomeric Li complexes. Most thin films that have been fabricated via ALD so far were prone to the formation of carbonates, which is often observed for Li containing films.[3]

In our present work we aim at opening pathways to solve the challenges with ALD of lithium containing materials. We propose a highly reactive heteroleptic and monomeric lithium precursor making use of the stabilizing effect of N-heterocyclic carbenes (NHC).

Identifying the stability of monomeric lithium complexes as generally troublesome, we adopted the proven technique of introducing a stabilizing ligand. When employing a NHC with its unique dative abilities due to the free electron pair, electron density can be provided to the electropositive lithium to decrease the strong polarization of the bond between Li and the HMDS ligand. When utilizing NHCs, a monomeric linear Li(I) complex [Li(NHC)(HMDS)] was successfully synthesized. This new complex has been characterized thoroughly by means of NMR, SC-XRD, and LIFDI-MS. Further, it shows excellent thermal properties as evidenced by the TGA (Fig. 1) as desired for ALD.

To prove its utility we set out to develop an ALD process and could successfully fabricate lithium silicate layers when the [Li(NHC)(HMDS)] is reacted with ozone as co-reactant. Self-limiting growth could be confirmed and XPS together with RBS/NRA were employed to prove the presence of both lithium and silicon oxide species, confirming the lithium silicate material. Making use of the specifically designed precursor, a new and valuable process for lithium-based materials could be realized. The present results set a new pathway in finding highly reactive and yet stable precursor chemistries to deposit Li-containing films by ALD.

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3:15pm **AF1-TuA-8 Benchmarking 4 Different Cobalt Precursors for Atomic Layer Deposition of Complex Cobalt Oxides***, **Yani Amedjkouh**, H. Sønsteby,*
University of Oslo, Norway

The world is in an energy crisis. In ICT, the demand for electricity is expected to jump up to 20% of today's production by 2030, mainly due to the rapid expansion of data centers and device networks. The main cause is the inefficiency of modern silicon technology in electronic devices. These devices are so inefficient in fact that 40% of the power use in a typical data center is spent on cooling. Moore's law has held true for over 50 years now but is beginning to fail. Silicon transistors cannot be much smaller than they already are, and therefore we need new materials with new functionalities. Oxides seem to be fit the bill for this purpose, as they host a wide variety of functional properties that have great potential for applications in electronics. The main issue holding these materials back is the lack of viable production methods at an industrial scale. This is where atomic layer deposition comes in. The big chipmakers already use ALD in their production lines, but what's missing are reliable ALD systems for complex oxides for the manufacturers to utilize. To achieve this, research into how different ALD precursors affect the systems is required.

The work we have done aims to serve as a benchmark for four cobalt precursors in a ternary cobalt oxide ALD system. The precursors in question are $Co(acac)_2$, $Co(acac)_3$, $Co(thd)_2$ and $Co(thd)_3$. We have chosen these four as they let us examine the difference between Co(II)- and Co(III)-precursors and the difference between having the larger thd-ligand and the smaller acac-ligand.

We have attempted to grow thin films of both binary cobalt oxide and the ternary $LaCoO_3$ to examine if the difference in precursor affects things as crystallinity, conformity, consistency, and growth rate as these things normally play an important role for the properties of the film material.

We have found that the crystal orientation of binary cobalt oxide deposited on α-Al_2O_3 substrates are affected by the choice of precursor. With the acac-precursors, we observe an additional set of reflections that are not present in films grown with the thd-precursors. Our belief is that the structure relaxes during growth only with the thd-precursors, and therefore we only observe one set of reflections. Furthermore, we have also observed that films grown with $Co(thd)_2$ have a lower growth rate than the rest, but virtually no thickness gradients in the reaction chamber.

It is our belief that the results we find will facilitate the development of novel ALD systems for complex cobalt oxides, as these materials exhibit both electric and magnetic properties.

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