ALD Fundamentals
Room Auditorium - Session AF1-MoA
New Precursors and Processes II

Moderators: Romain Gaillac, Air Liquide, Mikko Ritala, University of Helsinki

1:30pm **AF1-MoA-1 Atomic Layer Deposition of CsI and $CsPbI_3$,** ***Alexander Weiß****, G. Popov, E. Atosuo, P. Jalkanen, A. Vihervaara, M. Vehkamäki,* University of Helsinki, Finland*; H. Sipilä, A. Niemela,* Fenno-Aurum Oy Ltd, Finland*; M. Ritala, M. Kemell,* University of Helsinki, Finland

Cesium iodide (CsI) is one of the most studied and applied scintillator materials. It exhibits a band gap located in the UV region (5.42 eV) and an outstanding detective quantum efficiency (DQE). Owing to these properties CsI was established as material of choice for indirect x-ray imaging in radiology[1], amongst other applications. Moreover, CsI thin films are precursors to some halide perovskite absorbers that are used in Perovskite Solar Cells (PSCs). This young research field recently gained high interest because of the potential to deliver low-cost solar energy. However, there are still two challenges for PSCs to become widely commercially available: The difficulty in scaling-up and the instability of the perovskite in ambient conditions.

Our approach to tackle the scalability issue relies on Atomic Layer Deposition (ALD) because of its high controllability to deposit thin films on large areas and complex-shaped surfaces. We believe that developing an ALD process for CsI can also address the stability issue: Literature reports give evidence that perovskite solid solutions have better stability than pure perovskites. Key to these solid solutions is the controlled addition of several cations and/or anions into the perovskite structure. In our previous work, we already demonstrated an ALD process for PbI_2 thin films and its conversion into methyl ammonium lead iodide $CH_3NH_3PbI_3$ (MAPI)[2]. Developing an ALD process for CsI and combining it with the PbI_2 process to deposit $CsPbI_3$ would be the first step towards depositing solid solution perovskites with ALD from $CsPbI_3$ with MAPI.

In this work, we report a new ALD CsI process that uses cesium bis(trimethylsilyl) amide (Cs(btsa)) as the cesium precursor and tin(IV) iodide (SnI_4) as the iodine precursor. The high volatility of Cs(btsa) enables deposition of phase pure CsI at low temperatures (140 °C). In the range of 150 – 170 °C the process exhibits a temperature independent growth per cycle (GPC) value of 3.3 Å. The GPC saturates rapidly with respect to both precursor pulses and purge durations, and is independent of the number of deposition cycles. Furthermore, we demonstrate the deposition of ternary $CsPbI_3$ perovskite thin films with a two-step approach: First, we deposit CsI thin film via ALD. In the second step, the CsI film is exposed to our previous PbI_2 ALD process yielding directly $CsPbI_3$ perovskite. This combination of CsI and PbI_2 ALD allows to prepare phase pure γ-$CsPbI_3$ and δ-$CsPbI_3$ thin films, depending on the number of PbI_2 deposition cycles.

[1] Keiko et al. *U. S. Patent Appl. Publ.* **2011**. US20130068953A1

[2] Popov et al. *Chem. Mater.* **2019**, *31* (3), 1101-1109.

1:45pm **AF1-MoA-2 Co(II) Amide, Pyrrolate, and Aminopyridinate Complexes: Assessment of Structure and Thermal Properties as ALD Precursors***, **Jorit Obenlüneschloß**, D. Zanders,* Ruhr University Bochum, Germany*; M. Land, S. Barry,* Carleton University, Canada*; A. Devi,* Ruhr University Bochum, Germany

Thin films of cobalt metal are subject of high research and economic interest owing to their potential to facilitate performance increases in integrated circuitry (IC) devices at continuously shrinking dimensions. Its good conductivity and stability are among the reasons cobalt is handled as a replacement to copper. To implement cobalt thin films, atomic layer deposition (ALD) is a favorable fabrication technique allowing precise device architectures to be coated uniformly with sub nanometer thickness control.[1]

In ALD, the choice of precursor is of crucial importance because its thermal behavior and reactivity are paramount for successful deposition of a desired thin film material. Revisiting the library of Co precursors, all nitrogen coordinated precursor complexes are underexplored; surprisingly as Co(II) diazadienyls have successfully ventured into the field.[2]

Motivated by this premise, we studied a variety of new nitrogen coordinated Co complexes and their potential for ALD. They have been synthesized and thoroughly characterized by EA, EI-MS, SC-XRD, TGA and vapor pressure estimations.[3]

An entry point to this study was found in the Co(II) bis(trimethysilyl)amide dimer **1**. This very compound was reacted with a selection of amides, imides, amide-adducts, pyrroles, and amido-amines (Fig. 1). With structural and chemical ligand variations in the form of aromatic moieties, varying ring size, substitution patterns, bonding character and strategic incorporation of silylamide functionalities, a variety of cobalt compounds was successfully obtained (Fig. 1). The modifications were performed to gain a broader understanding of influences on reactivity, stability, and volatility with the aim of tailoring the compounds suitable for ALD.

Whereas some of the forwarded complexes followed the expected structural trends, others adopted distinctive and unexpected coordination motives (Fig. 2). This was reflected by their thermal behavior and underlined that gradual ligand alteration can have a vast impact Additionally, the assessment of volatility also shows distinct differences between the employed ligands (Fig. 3). Especially volatile with high stability were the Co(II) iminopyrrolate **9** and the silylamido-amine **11**. Those two newly uncovered precursors were found to be especially promising candidates for application in ALD process development.

[1] A. E. Kaloyeros, et al., *ECS J. Solid State Sci. Technol.***2019**, *8*, 119–152.

[2] J. P. Klesko, et al., *Chem. Mater.***2016**, *28*, 700–703.

[3] D. Zanders, J. Obenlüneschloß, et al., *Eur. J. Inorg. Chem.***2021**, 5119–5136.

2:00pm **AF1-MoA-3 SnO Thin Films *via* Water Based ALD using a Sn(II) Precursor: Precursor Evaluation and ALD Process Development***, **Niklas Huster**,* Ruhr University Bochum, Germany*; R. Ghiyasi,* Aalto University, Finland*; D. Zanders,* Ruhr University Bochum, Germany*; D. Rogalla,* RUBION, Ruhr University Bochum, Germany*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Tin(II) oxide is one of the few p-type semiconducting materials that possesses excellent electrical and optical properties. Hence this interesting material system is very appealing for applications in chemical sensing, as anode material for Li-ion batteries or as a transparent conductive oxide (TCO) in thin film transistor (TFT's), particularly due to the high hole mobility. Nevertheless, the deposition of stoichiometric SnO thin films is a challenging task. Atomic layer deposition (ALD) is a preferred process for thin film deposition as it is capable of yielding high quality, dense and uniform layers with an excellent control over film thickness as well as the ability to control the stoichiometry. Sn(II) oxide readily oxidizes to Sn(IV) and there are not many ALD processes known for obtaining highly stoichiometric SnO films. Thus, care must be taken with respect to process parameter selection and precursor choice.

Herein, we report the successful deposition of stoichiometric SnO thin films in a simple water based ALD process, employing the homoleptic, liquid tin(II) formamidinate precursor $[Sn(^iPr_2fAMD)_2]$ that was recently reported for ALD of SnS.[1]. Based on the promising thermal properties (Figure 1), good thermal stability and high reactivity towards water, we employed this precursor for ALD of SnO. The newly developed ALD process yielded SnO layers in the temperature range of 120 °C to 180 °C on Si substrates. The formation of tetragonal romachite-type SnO films was confirmed by Grazing Incidence X-ray Diffraction (GI-XRD) while surface and bulk composition were verified by means of X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS) / Nuclear Reaction Analysis (NRA) (Figure 2). The films were found to exhibit the desired stoichiometry alongside high purity. Optical bandgaps of as-deposited and annealed films were determined *via* Tauc-plotting from UV-Vis measurements. This is a very promising ALD process development where the role of precursor and co-reactant choice enabled the phase control of SnO films.

[1]Kim *et al.*, *ACS Appl. Mater. Interfaces*, **2019**, 11, 45892–45902

2:15pm **AF1-MoA-4 Tuning the Texture of ZnO Thin Films Through the Addition of a Volatile Shape-Directing Agent in the AP-SALD System***, C. Crivello, M. Weber,* LMGP Grenoble-INP / CNRS, France*; T. Jalabert, G. Ardila Rodriguez,* IMEP-LaHC UGA/CNRS/Grenoble INP, France*; M. Dibenedetto, **David Muñoz-Rojas**,* LMGP Grenoble-INP / CNRS, France

Zinc oxide draws attention for its relatively low cost, the wide bandgap of 3.37 eV,[1] and for its electrical and optical properties for applications such as gas sensors, solar cells, thin-film transistors and light-emitting diodes.[2,3] ZnO thin films can be obtained by different deposition methods, from sol-gel approach to sputtering, and gas-phases based approaches such as molecular beam epitaxy (MBE), chemical vapour deposition (CVD), atomic layer deposition (ALD).

Within the materials deposition techniques, Atmospheric Pressure Spatial ALD (AP-SALD) is gaining momentum since it is a high throughput and low-cost alternative to conventional ALD. AP-SALD is based on a physical separation (rather than temporal separation, as is the case in conventional ALD) of gas-diluted reactants over the surface of the substrate by a region containing an inert gas.[4]

In this presentation, we will show that a volatile shape-directing agent can be used to tune the texture and growth rate of ZnO thin films deposited by AP-SALD. While the use of such agents is common in liquid-based synthesis approaches, their use in the AP-SALD system has never been used to the best of our knowledge. (002)-oriented hexagonal wurtzite-type ZnO films were obtained at 200 °C, without any post-deposition treatment.

[1]Velázquez-Nevárez GA, Vargas-García JR, Aguilar-Hernández J, Vega-Becerra OE, Chen F, Shen Q, et al. Optical and Electrical Properties of (002)-Oriented ZnO Films Prepared on Amorphous Substrates by Sol-Gel Spin-Coating. Mater Res 2016;19:113–7. doi:10.1590/1980-5373-mr-2016-0808.

[2]Zhao M-J, Sun Z-T, Hsu C-H, Huang P-H, Zhang X-Y, Wu W-Y, et al. Zinc Oxide Films with High Transparency and Crystallinity Prepared by a Low Temperature Spatial Atomic Layer Deposition Process. Nanomaterials 2020;10:459. doi:10.3390/nano10030459.

[3]Dong J, Han D, Li H, Yu W, Zhang S, Zhang X, et al. Effect of Al doping on performance of ZnO thin film transistors. Appl Surf Sci 2018;433:836–9. doi:10.1016/j.apsusc.2017.10.071.

[4] Muñoz-Rojas D, Huong Nguyen V, Masse de la Huerta C, Jiménez C, Bellet D. Spatial Atomic Layer Deposition. Chem. Vap. Depos. Nanotechnol., IntechOpen; 2019. doi:10.5772/intechopen.82439.

2:30pm **AF1-MoA-5 Recent Advances in Rare Earth Precursors for ALD***, **Jean-Pierre Glauber**, M. Schmickler, P. Kaur, S. Beer, N. Boysen,* Ruhr University Bochum, Germany*; A. Devi,* Ruhr Universität Bochum, Germany

Rare earth (RE) containing thin films are indispensable for several different applications owning to their broad number of intrinsic functional properties. Especially, RE-oxides and -sulfides are of high interest for various applications such as high-κ dielectrics (Y_2O_3, CeO_2), optical fibers in lasers (Yb_2O_3), spintronics (EuS) or photovoltaics (Nd_2S_3). However, to gain fundamental insights and accelerate the development of these devices, reliable synthesis routes that yield high-quality material are required.[1] Vapor phase deposition methods such as atomic layer deposition (ALD) can meet these demands, but to develop promising processes for the formation of the RE-containing materials, precursors with certain pre-requisites are of utmost importance.[2] Besides sufficient volatility and thermal stability at the operating conditions, the precursors need to exhibit a high reactivity towards the employed co-reactant.

Commonly used ligands with oxygen-metal bonds suffer from a low reactivity towards the co–reactants due to strong RE–O bonds, which limits their applicability in ALD processes. On the other hand, precursors with guanidinate (dmg), amidinate (amd) and formamidinate (famd) ligand moieties have gained prominence since their all-nitrogen coordinated ligands ensure high reactivity toward mildly reactive co-reactants such as H_2O, while retaining volatility and thermal stability.[2,5]

Consequently, a series of RE containing precursors, with the formula $[M(L)_3]$ (M = Y, Ce, Eu, Yb; L = dpdmg, dpamd, dpfamd) were synthesized (Figure 1), structurally analyzed, and their thermal properties evaluated.[1-5] Furthermore, the tunability of the thermal properties via a variation of the ligand side chains was demonstrated for Y formamidinates [3] as well as for amidinates and guanidinates of Ce and Yb [2] with systematic thermogravimetric analysis studies (TGA).

Density functional theory (DFT) calculations of the reaction between selected Y, Yb and Ce precursors with H_2O revealed a pronounced reactivity towards mild oxidizing agents and underlined their suitability for ALD processes.[2,3] Actual ALD experiments of Y formamidinate- and Ce guanidinate-based precursors with H_2O as the co-reactant confirmed the results from DFT and yielded high-quality thin films of Y_2O_3 [3,4] (Figure 2) and CeO_2 [2], respectively. A high reactivity of the $[Eu(L)_3]$ (L = dpdmg, dpamd, dpfamd) towards O_2 and S_2 was obtained from DFT studies, further underlining the suitability of these ligand motifs in precursors for vapor phase deposition fabrication methods.[1]

2:45pm **AF1-MoA-6 Novel Growth Inhibitor in Atomic Layer Deposition for Conformal Coverage on High Aspect Ratio Trenches***, **Kok Chew Tan**, J. Jung, C. Yeon, S. Lee, J. Kim, J. Nam, T. Park, Y. Park,* Soulbrain, Korea (Republic of)

The continuous miniaturization of semiconductor devices has triggered growing interests in new strategy for depositing conformal coatings on complex geometry which are critical for device reliability. Despite ALD being a mainstream technique for conformal coatings, features with increasing aspect ratio have rendered this conventional ALD increasingly challenging to achieve the desired step coverage.

Various approaches have been conducted to improve film conformality and film quality on high aspect ratio (HAR) trenches such as screening of molecules with potential chemistry as inhibitor and tuning of ALD process parameters. In this work, we have narrowed down our approach by successfully identifying molecules with suitable chemistry (alkyl-halides) that could act as growth inhibitor in the first pulse step of ALD. This inhibitor enables the control of inherent kinetics of gas transport within the trenches by reducing the surface reactive sites for precursors on the top region while allowing more precursors to diffuse deeper into the trenches, thus improving film conformality in high aspect ratio trenches. Besides growth inhibition, the selected inhibitor could function as film quality enhancer and could also be easily removed during reactant pulse step without contaminating the films.

By leveraging the selected inhibitor chemistry and ALD deposition characteristics, our approach has demonstrated significant improvement in TiN film conformality to 90% in HAR trench features, as determined by the ratio of bottom side film thickness to top side film thickness **[1]**. In terms of film resistivity, an observable 50% improvement was obtained owing partially to large decrease in Cl impurity as determined by SIMS depth profiles **[1]**. The introduction of inhibitor has also exhibited promising benefits in the ALD of high-*k* dielectric film, HfO_2. Improvement in HfO_2 film conformality to 97% in HAR trench features as well as significant improvement of 95% in leakage current due to enhancement in film quality were simultaneously observed **[2]**.

Based on these experimental evidences, our approach has been proven its promising potential as an innovative solution to address the challenges of depositing highly conformal films of excellent quality on high aspect ratio features such as DRAM trench capacitor and 3D NAND.

References:

1. C. Yeon, J. Jung, H. Byun, K.C. Tan, T. Song, S. Kim, J.H. Kim, S.J. Lee and Y. Park, AIP Advances 11, 015218 (2021).
2. K.C. Tan, J. Jung, S. Kim, J. Kim, S.J. Lee and Y. Park, AIP Advances 11, 075008 (2021).

3:00pm **AF1-MoA-7 Solution ALD: A Versatility Process for the Growth of Sulfides and Selenides***, **Maissa Barr**, B. Zhao, P. Von Grundherr,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; V. Koch,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; J. Charvot ,* University of Pardubice: Pardubice, CZ, Czechia*; M. Halik,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; F. Bureš,* University of Pardubice, Czechia*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

We have proposed and demonstrated a novel thin film deposition technique by transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, towards precursors dissolved in a liquid. The technique can also be considered as a generalization of already established methods such as the 'layer by layer' growth or the 'successive ion layer adsorption and reaction' (SILAR). 'Solution ALD' (sALD) shares the fundamental properties of standard 'gas ALD' (gALD), specially the self-limiting growth and the ability to coat conformally deep pores. It has been already shown that it is possible to transfer standard reactions from gALD to sALD such as TiO_2 deposition . However, sALD also offers novel opportunities such as overcoming the need for volatile and thermally robust precursors.

To illustrate this, we establish sALD procedures for depositing films of non oxides layers such as Pb-compound deposition, MOF, selenides and sulfides. Those examples highlight how ionic, polar, or high-molecular weight precursors that only exist in the condensed phase are now rendered amenable to being utilized in surface-controlled thin film formation by sALD for depositing materials that would otherwise be more difficult or more expensive to achieve by gALD or hazardous. The deposition was achieved on small (2 cm*1 cm) and large samples (up to 10 cm*10 cm). The ALD behavior has been shown. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition has been investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. Additionally, the nucleation is studied in function of chemical pretreatment to control the growth and allow selective deposition of SnS, SnSe and Sb_2Se_3.

This particular ALD process offer the growth of high quality and crystalline layers in middle conditions with the use of low cost and environmental friendly precursors.

Y. Wu, D. Döhler, M. Barr, E Oks,M. Wolf, L. Santinacci and J. Bachmann, Nano Lett. **2015**, *15*, 6379

J. Fichtner, Y. Wu, J. Hitzenberger, T. Drewello and J. Bachmann, ECS J. Solid State Sci. Technol. **2017**, *6*, N171

3:15pm **AF1-MoA-8 Flash-Lamp Enabled Atomic Layer Deposition***, **Martin Knaut**, Y. Cui, R. Deltschew, M. Albert, T. Mikolajick,* TU Dresden, Germany

Atomic layer deposition (ALD) processes are widely used in research and development as well as in various production environments. Nowadays, a variety of materials can be deposited using thermal and energy enhanced atomic layer deposition but there are limits that are mainly set by the properties of available precursors and the related processes. Besides the necessity of suitable precursors and chemical reactions to deposit a specific material, there are two major limitations: the thermal self-decomposition of precursor molecules which can be in conflict with the required process temperatures enabling desired film properties, and the typical temperature-related reactivity of precursors and co-reactants with substrate materials. These can affect the initial film growth and can lead to adhesion issues and unwanted interface layers, such as oxides formed by oxidizing agents used during the ALD process.

We developed a novel flash lamp enabled atomic layer deposition (FLE-ALD) process to address these limitations of common ALD processes. The process combines the self-limiting chemisorption of precursor molecules in the first half-cycle with a millisecond flash lamp anneal (FLA) during the second half-cycle. The heat applied during the second process step enables single-source ALD processes by inducing a thermal decomposition of chemisorbed molecules resulting in the desired film material.

This paper demonstrates the FLE-ALD approach for the deposition of oxide and nitride films in single-source processes combining metal organic precursor exposures with flashes of optical light with a duration in the millisecond range to heat a surface for a very short time and to decompose the chemisorbed molecules. The heat induced by the short FLA step is distributed into the substrate’s bulk and the process chamber during the subsequent purging step, resulting in a constant substrate temperature and maintaining the self-limiting behavior of the precursor chemisorption.

The process development confirmed the FLE-ALD principle and the ALD typical self-limiting and constant growth per cycle by varying and characterizing process parameters like precursor dose, purge times, flash lamp energy, substrate temperature, and cycle number. Spectroscopic ellipsometry was used to measure the film thicknesses and to investigate the optical properties of the deposited films. The film composition was measured by X-ray photoelectron spectroscopy and scanning electron microscopy was used to analyze step coverage in high aspect ratio structures.

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