## ALD Fundamentals
## Room Grand Ballroom E-G - Session AF1-TuM

### Precursors and Processes I

**Moderator:** Prof. Dr. Charles H. Winter, Wayne State University

8:00am **AF1-TuM-1 Precursor Design Enabling Angstrom Era Semiconductor Manufacturing*, Charles Mokhtarzadeh*,** *E. Mattson, S. Lee, S. Clendenning, P. Theofanis,* Intel Corporation **INVITED**

The ever more challenging dimensions and architectural complexity of nanofabricated structures in the semiconductor industry and beyond are often combined with the need for new materials. This drives the need for the chemist and the thin films deposition engineer to innovate across the periodic table. For example, recent advances in the Gate All Around (GAA) RibbonFET transistor technology characteristic of the Angstrom Era of semiconductor manufacturing necessitate the use of atomic layer deposition in high aspect ratio complex spaces and are also creating opportunities for atomic layer etch and selective deposition. At the heart of this is a need for new precursor and thin films chemistry. Taking a survey of well-established ALD precursors as a starting point, we will consider new ligand scaffolds and the synthesis of derived precursors and thin films. Approaching thin films from an etch point of view, we will look at how non-traditional ligands can be used for the ALE of industry relevant films. Lastly, some perspective will be provided on precursor design and synthesis as key elements in meeting future manufacturing needs

8:30am **AF1-TuM-3 Atomic Layer Deposition of Silver Halides*, Georgi Popov*,** *T. Hatanpää, A. Weiß, M. Chundak, M. Ritala, M. Kemell,* University of Helsinki, Finland

Although AgCl, AgBr and AgI have unique attractive properties, our primary motivation for developing ALD processes for these materials is the deposition of silver halide perovskites. Silver halides are IR-transparent and antiseptic, which has enabled their use in niche optical and medical applications. Silver halides are also light-sensitive, which we believe can be exploited for patterning applications. Most importantly, silver halides are components of double perovskites, such as $Cs_2AgBiBr_6$.

Halide perovskites are a major topic in materials science and are associated with Pb compounds, photovoltaics, and challenges with scalability, stability, and toxicity. However, one-third of the publications on perovskites are unrelated to photovoltaics. The largest and fastest growing non-photovoltaic applications of perovskites are light-emitting diodes, sensors, and microelectronic components. In these applications, it is possible to use Pb-free alternatives like double perovskites. Silver and bismuth double perovskites, like $Cs_2AgBiBr_6$, are stable and nontoxic, eliminating two of the three challenges.[1] Depositing double perovskites with ALD could address the remaining scalability challenge.

The development of ALD processes for ternary and quaternary compounds begins with the processes for the corresponding binary compounds. From our previous work[2] we know how to deposit cesium halides, but no processes for silver and bismuth halides are known. This work focuses on silver halide processes using Ag(fod)($PEt_3$), a silver precursor well established in the ALD and CVD of metallic silver.

Our metal-halide ALD processes employ volatile metal halides, like $SnI_4$, as halide precursors. In our previous work, we discovered that the choice of the volatile metal halide makes or breaks the process.[3] The byproducts generated by the volatile metal halide can be benign or detrimental by being able to etch the film material or by being nonvolatile, which results in the incorporation of impurities and poor crystallinity. Therefore, we screened the candidates to identify suitable pairs. The candidates are the corresponding halides of titanium, gallium and tin.

For example, Ag(fod)($PEt_3$) and $SnI_4$ are one such pair. These precursors produce crystalline β-AgI films in the 100 – 200 °C temperature range with the largest GPC of 0.9 Å at 140 °C. The films were smooth, uniform, and contained a negligible amount of impurities. We continue our process studies on suitable precursor pairs for the other silver halides.

[1] Lei et al., *Adv. Funct. Mater.* **2021**, 31, 2105898.

[2] Weiß et al., *Chem. Mater.* **2022**, *34*, 6087.

[3] Popov et al., *Dalt. Trans.* **2022**, *51*, 15142.

8:45am **AF1-TuM-4 Novel Metal Fluoride ALD Processes*, Elisa Atosuo*,** *M. Mäntymäki, M. Heikkilä, K. Mizohata, M. Leskelä, M. Ritala,* University of Helsinki, Finland

The number of ALD processes for metal fluorides has been limited, especially when compared to ALD processes for metal oxides, nitrides, and sulfides. Recently, however, interest towards ALD of metal fluorides has increased. The applications for metal fluoride films range from optical coatings to lithium-ion batteries (LIB) and luminescence devices. This work summarizes recent studies on ALD of metal fluorides at University of Helsinki.

New ALD processes for rare earth and transition metal fluorides are presented. Of the rare earth metal fluorides, we have included an ALD process for $ScF_3$, which is a negative thermal expansion (NTE) material. To our knowledge, this is the first wide-temperature range NTE material deposited by ALD. The films are close to the stoichiometric, and, e.g., in films deposited at 300 °C the total impurity content (O, C, and H) is only ~2.6 at-% as measured by ToF-ERDA. In addition, an ALD process for $GdF_3$ and its *in-situ* conversion to $NaGdF_4$ by Nathd (thd=2,2,6,6-tetramethyl-3,5-heptanedione) are presented. $GdF_3$ is an important material for antireflection coatings, whereas $NaGdF_4$ is a potential host material for luminescence centers, especially for medical applications. Of the transition metal fluorides, an ALD process is presented for $CoF_2$ that is a potential LIB cathode material.

In addition to the new metal fluoride ALD processes, we introduce a new fluoride source, $NbF_5$, the use of which has been inspired by the successful use of $TiF_4$ and $TaF_5$ as fluoride sources in ALD. In this work $NbF_5$ was combined with $Ho(thd)_3$ to deposit $HoF_3$. In $HoF_3$ films, Nb impurity content as low as 0.2 at-% was obtained.

We aim to give a comprehensive overview of ALD of metal fluorides. Therefore, also future research directions will be discussed.

9:00am **AF1-TuM-5 Halide-free, Low Melting, Volatile, Thermally Stable Mo(0) Precursors for ALD of Mo films**, *C. Barik, A. Leoncini,* Applied Materials – National University of Singapore Corporate Lab, Singapore*; F. Liu,* Applied Materials, Inc.*; J. Tang, J. Sudijono,* Applied Materials – National University of Singapore Corporate Lab, Singapore*; M. Saly,* Applied Materials, Inc.*; **Chandan Das**,* Applied Materials, Inc., Singapore

State-of-the-art devices require surrounding Cu interconnects with a layer of tantalum (Ta liner) and a layer of tantalum-nitride (TaN barrier) to prevent diffusion of Cu atoms into the surrounding dielectric, which is detrimental to the lifetime of the IC. Downscaling of integrated circuits (ICs) faces significant challenges because the resistivity of Cu features increases at smaller dimensions according to the product $\lambda\times\rho_0$, and further thinning of the Ta/TaN layers would result in increased resistivity and poorer performance. Among metals with lower $\lambda\times\rho_0$ values, cobalt (Co) requires a barrier film and ruthenium (Ru) is difficult to process during CMP. Molybdenum (Mo), which does not require a barrier and is CMP processable, is a suitable alternative for Co and Ru and the entire Cu/Ta/TaN interconnect. Current commercial processes use solid halide-based precursors ($MoCl_5$ and $MoO_2Cl_2$). As device integration becomes more complex with each node generation, halide-free deposition processes are necessary. We designed and successfully synthesized a halide free Mo precursor with small ligands, which is low melting and has high volatility. We studied its thermal stability, volatility and chemical properties. Our precursor consists of a) Mo at zero oxidation state, b) neutral halide-free ligands – easier to detach from metal thermally during deposition.

We synthesized and characterized our precursor by $^1H$-, $^{13}C$- and $^{31}P$- NMR spectroscopy, and its molecular structure has been confirmed by x-ray crystallography. Its low-melting point (35 °C) makes it easy to handle and enables liquid delivery. Thermogravimetric analysis shows good volatility, with $T_{½}$ 173 °C and low residual mass. The thermal stress analysis showed that it is stable at 200 °C for at least 7 days (Figure 1b). The clean TGA profile with ~1% residue after annealing indicates its thermal stability. Moreover, the isothermal TGA at 100 °C indicates that the chemical is volatile and deliverable to the reaction chamber (Figure 1c). The precursor was also employed for ALD and CVD deposition of Mo-rich films, and we investigated how the film composition responded to different deposition conditions.

9:15am **AF1-TuM-6 Thermal Atomic Layer Deposition of MoC Thin Films*, Paloma Ruiz Kärkkäinen*,** *T. Hatanpää, M. Heikkilä, K. Mizohata, M. Chundak, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Transition metal carbides (TMCs) are widely used in catalytic and wear resistance applications. They exhibit excellent chemical and thermal stabilities, exceptional hardnesses, and low resistivities. Additionally, TMCs typically have good electromigration resistances. These properties make them relatively good conductors for metal wires when the dimensions shrink to the sub-10 nm range. Development of TMC ALD processes opens the possibility to use carbides in semiconductor applications. Molybdenum carbides ($MoC_x$) have the potential to improve the performance, efficiency, and reliability of semiconductor devices. Recently, they have emerged as potential candidates for diffusion barriers, interconnects, and gate electrodes.[1–3] The ALD of metal carbides is, however, still in its infancy, and current challenges include a lack of thermal ALD processes, high process temperatures, and low growth rates.

In this work, we report a novel thermal ALD process for MoC with $MoCl_5$ and bis(trimethylgermyl)-1,4-dihydropyrazine ($(Me_3Ge)_2DHP$) as precursors. $(Me_3Ge)_2DHP$ has previously been used as a reducing agent in ALD of nickel and gold.[4,5] In the current process, $(Me_3Ge)_2DHP$ acts as both the reducing agent and carbon source for the first time. The process was investigated at temperatures between 200 and 300 °C. At 275 °C, high growth rates of 1 Å/cycle were observed. The films are very smooth with XRR roughnesses of approximately 0.25 nm. The growth rate is strongly affected by the $MoCl_5$ pulse length, and we observed a small etching component by $MoCl_5$ in all depositions. Remarkably, according to XPS the MoC films do not contain any metallic Mo. The resistivities of the moderately crystalline films are ~200 μΩcm at a film thickness of ~100 nm, which is slightly higher than those for bulk $MoC_x$. No change in the crystallinity was observed after annealing up to 1000 °C under $N_2$ atmosphere. The influence of process parameters on the MoC film properties as well as the mechanism of the process is discussed in detail.

[1] Tripathi, C. C., *et al. Appl. Surf. Sci.* **255**, 3518–3522 (2009). https://doi.org/10.1016/j.apsusc.2008.09.076.

[2] Leroy, W. P., *et al. J. Appl. Phys.* **99**, 063704 (2006). https://doi.org/10.1063/1.2180436.

[3] Ha, M.-J. *et al. Chem. Mater.* **34**, 2576–2584 (2022). https://doi.org/10.1021/acs.chemmater.1c03607.

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

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

9:30am **AF1-TuM-7 Precursors and Processes for the Atomic Layer Deposition of Bismuth Metal Thin Films***, **Daniel Beh,*** Wayne State University*; Z. Devereaux, T. Knisley,* Applied Materials*; C. Winter,* Wayne State University

The element bismuth (Bi) is an important component of materials ranging from insulators to superconductors. For many applications, thin films containing Bi need to be grown in high aspect ratio features with perfect conformality and Angstrom-level thickness control. Atomic layer deposition (ALD) is a film growth method that can afford uniform thickness films, even in narrow and deep nanoscale features. While Bi ALD precursors have been reported for materials such as oxides,[1] there have been no reports to date of the ALD growth of Bi metal films. Herein, we will describe a family of thermal ALD processes for Bi metal thin films. Bi precursors used in this work include $BiCl_3$, $BiPh_3$, and $Bi(NMe_2)_3$. Reducing co-reactants fall into two general classes. Processes with $BiCl_3$ and 2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene (**1**) or 1,4-bis(trimethylsily)-1,4-dihydropyrazine (**2**)[2] afforded Bi metal films at substrate temperatures ranging from 50 to 175 ºC. Here, **1** and **2** serve as the reducing agents, with elimination of $Me_3SiCl$ and toluene (**1**) or pyrazine (**2**). ALD processes were also developed using $BiCl_3$, $BiPh_3$, or $Bi(NMe_2)_3$ in combination with nitrogen sources such as ammonia, hydrazine, alkyl hydrazines, or alkyl amines. The processes with nitrogen-based co-reactants are proposed to proceed via the formation of unstable "BiN", which decomposes to afford Bi metal films. All of these processes afforded crystalline Bi metal films, as determined by X-ray diffraction. X-ray photoelectron spectroscopy demonstrated that the films were >94% pure Bi metal after argon ion sputtering to remove adventitious surface impurities.

1. For example, see: Hatanpää, T.; Vehkamäki, M.; Ritala, M.; Leskelä, M. *Dalton Trans.***2010**, *39*, 3219-3226.

2. Klesko, J. P. Thrush, C. M.; Winter, C. H. *Chem. Mater.***2015**, *27*, 14, 4918–4921.

9:45am **AF1-TuM-8 Atomic Layer Deposition of Tin Oxide Thin Films Using a New Liquid Precursor Bis(ethylcyclopentadienyl) Tin***, **Makoto Mizui,** N. Takahashi, F. Mizutani,* Kojundo Chemical Laboratory Co., Ltd., Japan*; T. Nabatame,* National Institute for Materials Science, Japan

Transparent conductive oxide thin films, including SnO, $SnO_2$, In-Sn-O (ITO), Zn-Sn-O (ZTO), and In-Zn-Sn-O (IZTO) films, have recently attracted much attention for various applications such as flat-panel displays, gas sensors, and solar cells. We have reported the atomic layer deposition (ALD) of $In_2O_3$ and ZnO thin films using cyclopentadienyl-based precursors [1, 2]. In order to deposit such transparent conductive oxide thin films by using ALD, ALD-Sn precursor is essential. This time, we report ALD of tin oxide ($SnO_x$) thin films using a new liquid cyclopentadienyl-based precursor.

As a new ALD-Sn precursor, bis(ethylcyclopentadienyl) tin, $Sn(EtCp)_2$, was synthesized. $Sn(EtCp)_2$ is a liquid precursor at room temperature. Differential scanning calorimetry (DSC) was conducted to measure its thermal decomposition temperature. The decomposition temperature was estimated approximately 230 °C, so the deposition temperature was set to 200 °C, which is the same temperature in the case of ALD of $In_2O_3$ and ZnO thin films [1, 2]. The vapor pressure of $Sn(EtCp)_2$ was determined by directly measuring the equilibrium vapor pressures at several points. From the Clausius-Clapeyron plot for $Sn(EtCp)_2$, the precursor temperature was set to 70 °C, which corresponds to the vapor pressure of approximately 0.8 Torr.

$SnO_x$ thin films were deposited on 150 mm Si wafers with native oxide films. ALD process was conducted by using $Sn(EtCp)_2$ as a precursor and $O_2$ plasma as an oxidant. Saturation of reaction was confirmed when 14 s of $Sn(EtCp)_2$ and 45 s of $O_2$ plasma pulse times were applied. At this condition, linear growth of $SnO_x$ thin film was observed. The growth per cycle (GPC) was approximately 0.18 nm/cycle with this ALD condition. This growth rate was relatively fast compared with a previous experiment using tetrakis(dimethylamino)tin (TDMASn) as a precursor and $O_2$ plasma as an oxidant (~0.13 nm/cycle) [3]. On the contrary, by applying $H_2O$ for 30 s in the place of $O_2$ plasma, the thickness of $SnO_x$ films scarcely increased by increasing the number of ALD cycles.

$SnO_x$ thin films were deposited by ALD using a new cyclopentadienyl-based precursor $Sn(EtCp)_2$, and linear growth of $SnO_x$ thin film was confirmed.

**References**

[1] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, AIP Advances **9,** 045019 (2019).

[2] F. Mizutani, M. Mizui, N. Takahashi, M. Inoue, and T. Nabatame, ALD2021, AF1-10 (2021).

[3] M. A. Martínez-Puente, J. Tirado, F. Jaramillo, R. Garza-Hernández, P. Horley, L. G. S. Vidaurri, F. S. Aguirre-Tostado, and E. Martínez-Guerra, ACS Appl. Energy Mater. **4,** 10896 (2021).

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