ALD Fundamentals
Room Tamna Hall BC - Session AF2-MoA
Precursor Chemistry I

Moderators: Seán Barry, Carleton University, **Haripin Chandra**, The Electronics business of Merck KGaA Darmstadt

4:00pm **AF2-MoA-11 The Emergence of New Ligands for ALD Precursor Development***, **Anjana Devi**,* Leibniz Institute for Solid State and Materials Research, Germany **INVITED**

Advances in atomic layer processing of functional materials crucially depend on the progress made in precursor development. Without persistent research on precursors, atomic layer deposition (ALD) technology would not be the fastest growing thin-film technology in microelectronics industry or could not expand towards new emerging applications in nanotechnology and energy sector. The beneficial properties of ALD namely low temperature processing, conformal coverage, composition control can be exploited if the precursors and the co-reactants are fine-tuned to achieve the desired film properties. The understanding of precursor chemistry and their design and synthesis concepts needs specific attention. In this presentation, the recent research in ligand design and ALD precursor chemistry that governs layer formation and thin film characteristics for different material systems will be discussed. One representative example is using dimethylamino-propyl (DMP) ligand for various metals (Al, Zn, Ru, Mg). It not only serves as effective ligands for metalorganic precursor synthesis, but DMP-based compounds can be used as intermediates as well as reducing agents for metal deposition implying the broad applicability of the DMP ligand. The chelating nature of the DMP ligand furthermore yields sterically and electronically saturated metal centers, enabling the formation of monomeric complexes with enhanced volatility. The emergence of the DMP ligand system has also resulted in developing non-pyrophoric metal precursors that are suitable for temporal ALD, plasma ALD and spatial ALD applications. These findings reveal the promising potential of ligand engineering towards precursor development to meet the demands of materials for advanced technological applications.

4:30pm **AF2-MoA-13 A Novel Liquid Cocktail Precursor for Atomic Layer Deposition of Hafnium-Zirconium-Oxide Films for Ferroelectric Devices***, **Akihiro Nishida**, Tsukasa Katayama, Takashi Endo, Yasutaka Matsuo,* Hokkaido University, Japan

$Hf_xZr_{1-x}O_2$ (HZO) thin film is a promising material for next-generation ferroelectric memory devices. Ferroelectric HZO films are industrially produced using atomic layer deposition (ALD) technique. However, conventional ALD precursors for ZrO_2 exhibit lower thermal stability than those for HfO_2; thus, the deposition temperature is limited by the Zr precursor processing temperature (320 °C), limiting the quality of HZO.[1] In this study, we developed a novel ALD precursor for HZO: a liquid homoleptic cocktail precursor referred to as FER-1, which is composed of tetrakis(1-(*N*,*N*-dimethylamino)-2-propoxy)hafnium [$Hf(dmap)_4$] and tetrakis(1-(*N*,*N*-dimethylamino)-2-propoxy)zirconium [$Zr(dmap)_4$] in a 1:1 mol% mixture.(Fig. 1) Both $Hf(dmap)_4$ and $Zr(dmap)_4$ are stable at temperatures as high as 371 °C. In addition, these compounds have a similar vapor pressure (Fig. 2), similar ALD window, and excellent mixture stability. Furthermore, FER-1 is a volatile compound that shows a very clean thermogravimetry curve without decomposition or residue formation at 10 Torr. (Fig. 3) The ALD window was estimated to range from 300 to 360 °C. (Fig. 4) This is the first report of ALD of HZO film using cocktail precursor greater than 320 °C. Interestingly, the Hf/Zr concentration ratio of the HZO film prepared using FER-1 was the same as the Hf/Zr concentration ratio in the precursor mixture, demonstrating that the Hf/Zr composition can be easily controlled.MIM TiN/HZO/TiN devices were fabricated to evaluate the ferroelectric properties of the HZO films. The remanent polarization $2P_r$ reached 36.9 $\mu C/cm^2$.(Fig. 5) The *C*–*V* curve of the HZO film exhibits butterfly-shaped hysteresis loop, indicating the ferroelectric nature of the film. The dielectric constant of HZO film was varied in the range of 35.5–40.8 by voltage sweep. (Fig. 6) Our findings show that FER-1 is a highly useful ALD precursor for industrial HZO production.

References

1. H. B. Kim et al., Nanoscale 2021 Vol. 13 Issue 18 Pages 8524-8530

4:45pm **AF2-MoA-14 Anhydrous Hydrogen Iodide Source for ALD of CsI and Other Metal Halides***, **Georgi Popov**, Alexander Weiß, Anton Vihervaara, Kenichiro Mizohata, Mikko Ritala, Marianna Kemell,* University of Helsinki, Finland

Metal halides are an emerging group of compounds with a steadily increasing number of ALD processes published each year.[1] Most metal halide ALD processes employ volatile metal halides, such as TiX_4 or SnX_4, as halide (X = F, Cl, Br, I) precursors. ALD processes were first developed for metal fluorides using HF, with a later transition towards volatile metal fluorides (for example, TiF_4 and TaF_5) as safer and less corrosive alternatives to HF. The main applications of metal fluoride films are in optics and batteries.

Among metal halides other than fluorides, the main interest is in iodides, motivated by the desire to deposit halide perovskites with ALD. Halide perovskites are primarily iodides that exhibit outstanding performance in solar cells and several other applications. Existing ALD processes for iodides use volatile metal iodides as iodine precursors. For instance, SnI_4 acts as an iodine source in the ALD process for $CsPbI_3$ perovskite.[2] SnI_4 as an iodine source contaminates the film with Sn, which is detrimental for halide perovskite applications. Furthermore, Sn compounds are not relevant for photovoltaic industry due to their high costs and supply chain risks.[3]

Anhydrous hydrogen iodide (HI) gas is the least expensive, simplest, and most straightforward iodine precursor to deliver and use. HI does not suffer from issues related to metal halides, such as SnI_4. However, HI is not commercially available, likely due to a lack of industrial demand. We contacted many gas and chemical suppliers during 2015 – 2019, but none were willing to supply HI.

In this work we demonstrate a source design that produces anhydrous HI gas on-site. The source is constructed from catalogue vacuum parts with a total cost of less than 1000 USD and uses inexpensive common bulk chemicals (ca. 20 USD to fully fill the source). To demonstrate the feasibility of this source, we developed a new ALD process for CsI using Cs(btsa) (cesium(I)bis(trimethylsilyl)amide) and HI. Using this chemistry, CsI can be deposited over a wide temperature range of 150 – 325 °C. GPC is independent of the deposition temperature within 150 – 200 °C and 250 – 300 °C. The deposited CsI films are uniform, crystalline, and pure. Furthermore, cost analysis showed a 40% decrease in the CsI ALD process cost with our HI source compared to SnI_4.

1. Leskelä et al., AVS 70th International Symposium, Nov. **2024**, Tampa, FL.

2. Weiß et al., Chem. Mater. **2022**, 34, 13, 6087.

3. Schileo and Grancini, *J. Mater. Chem. C,* **2021**, *9* (1), 67–76.

5:00pm **AF2-MoA-15 Evaluating Trisilylamine and Diiodosilane as Silicon Precursors for PEALD of Silicon Nitride in Front-End-of-Line Applications***, **Keerthi Dorai Swamy Reddy**, Marco Lisker,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany

The ubiquitous use of Silicon Nitride (SiN) in front-end-of-line (FEOL) applications such as spacers, etch stop layers, optical waveguide materials, and trench liners has made it essential to develop deposition methods meeting its stringent requirements. Well-established techniques like low-pressure chemical vapor deposition (LPCVD) and plasma-enhanced chemical vapor deposition (PECVD) have successfully addressed many of the film property constraints for specific applications. However, the rapid miniaturization of devices has shifted the focus towards achieving conformality and uniformity at lower deposition temperatures, making Plasma-enhanced atomic layer deposition (PEALD) the most suitable method.

Following the choice of deposition method, the selection of precursors plays a critical role in determining key film properties, such as the impurity content, stoichiometry, density, and etch rate. These layer properties, in turn, significantly influence the electrical characteristics of devices. In addition to meeting the requirements for film properties, the chosen precursors must also enable an economical process to ensure the feasibility of high-volume manufacturing. For PEALD, halides, aminosilanes, or silylamines are typically used as Si precursor sources. In this study, we compare two Si precursors, namely, Trisilylamine (TSA) and Diiodosilane (DIS), in terms of PEALD process development parameters and their corresponding film properties, aiming to achieve an economical process suitable for FEOL applications.

In this work, a direct plasma ALD tool was used to compare the deposition process of SiN at 250 °C. For TSA, a combination of Nitrogen and Hydrogen plasma was used as a co-reactant, whereas for DIS, nitrogen plasma alone served as the co-reactant. In both cases, Argon was used as the carrier gas. The SiN process development was initially studied for both precursors by varying the respective PEALD process parameters. A comparison of ALD cycle time, precursor pulse time, growth rate per cycle, precursor consumption, and economic value of the precursors for the layer growth is presented in Table 1 (in PDF). The etch rates of as-deposited and annealed films in two different etchants are compared in Table 2 (in PDF). Additionally, the average refractive index, uniformity, conformality, and stoichiometry are compared. For device applications, key electrical characteristics such as breakdown voltage and leakage current are also compared. Although both TSA and DIS-based films result in uniform and conformal films, TSA appears to be a better suitable candidate for SiN deposition due to its lower precursor consumption and better economic value.

5:15pm **AF2-MoA-16 Precursor Design for Thermal ALD of Silver Metal***,* ***David Emslie****, Nick Hoffman,* McMaster University, Canada

Thin films of metallic silver are of interest as transparent electrodes for solar cells and LEDs,[1] and in photonics/plasmonics.[2] ALD is a uniquely capable method for the deposition of highly uniform and conformal thin films, and a handful of methods for silver thermal ALD have previously been reported. For example, several publications describe the use of [(hfac)Ag(COD)] (hfac = hexafluoroacetylacetonate; COD = 1,5-cyclooctadiene) as a precursor for Ag ALD, in combination with ^{n}PrOH[3-5] or ^{t}BuNHNH$_2$[4] as the co-reactant. However, the [(hfac)Ag(COD)] precursor is thermally unstable and requires direct liquid injection, and the reported processes exhibit a narrow (5–23 °C) temperature window. ALD methods have also been reported using [(hfac)Ag(PMe$_3$)] (Me = methyl) in combination with formalin ($H_2C=O/H_2O$),[6] or in a multi-step process involving reactions with AlMe$_3$ and then H_2O.[6] However, these methods afforded nanoparticles rather than continuous films. Finally, thermal ALD of Ag has been achieved using [(fod)Ag(PEt$_3$)] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) with BH$_3$(NHMe$_2$), affording films with a matte finish due to a rough microstructure.[7]

This presentation will describe the synthesis of a family of new silver alkoxide complexes, $[\{L_xAg(OR)\}_n]$ (L = PR'$_3$, CNR', NHC; R = $C(CF_3)_3$ or $C(CH_3)_3$; R' = Alkyl; NHC = N-heterocyclic carbene), comparison of their solid-state structures, volatility, melting points, and thermal stability, their solution reactivity with potential ALD co-reactants, and thermal ALD of silver metal using one of the precursors.

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Author Index

Bold page numbers indicate presenter

— D —
Devi, Anjana: AF2-MoA-11, **1**
Dorai Swamy Reddy, Keerthi: AF2-MoA-15, **1**
— E —
Emslie, David: AF2-MoA-16, **2**
Endo, Takashi: AF2-MoA-13, 1
— H —
Hoffman, Nick: AF2-MoA-16, 2
— K —
Katayama, Tsukasa: AF2-MoA-13, 1
Kemell, Marianna: AF2-MoA-14, 1
— L —
Lisker, Marco: AF2-MoA-15, 1
— M —
Matsuo, Yasutaka: AF2-MoA-13, 1
Mizohata, Kenichiro: AF2-MoA-14, 1
— N —
Nishida, Akihiro: AF2-MoA-13, **1**
— P —
Popov, Georgi: AF2-MoA-14, **1**
— R —
Ritala, Mikko: AF2-MoA-14, 1
— V —
Vihervaara, Anton: AF2-MoA-14, 1
— W —
Weiß, Alexander: AF2-MoA-14, 1