ALD Fundamentals
Room Tamna Hall BC - Session AF3-TuM

Precursor Chemistry II

Moderators: Venkateswara Pallem, AirLiquide, **Paul Williams**, Pegasus Chemicals

8:15am **AF3-TuM-2 ALD of SnO_2 Thin Films using Tin(IV) Acetate as a Novel Precursor*, Anjan Deb*,** *Miika Mattinen, Mikko J. Heikkilä, Mykhailo Chundak, Anton Vihervaara, Kenichiro Mizohata, Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

Tin dioxide (SnO_2), with an exceptional combination of high transparency, conductivity and stability in harsh chemical environments, has gained a lot of attention as a potential material for various optoelectronic applications including transparent electrodes for solar cells, anode materials for batteries, smart windows and displays, gas sensing and catalysis. Many of these applications require scalable, highly uniform and conformal thin films with superior quality and performance. The atomic layer deposition (ALD) technique offers a unique combination of scalability, uniformity and conformality with angstrom level thickness control.

Most of the previously studied ALD precursors for SnO_2 require highly oxidizing coreactants, such as O_3, H_2O_2, and O_2 or H_2O plasma. These processes are unsuitable for various sensitive applications, including biological systems and polymeric substrates. Among the available precursors, $SnCl_4$ and tetrakis(dimethylamino)tin(IV) react with water; however, $SnCl_4$ presents challenges due to the high deposition temperatures (300–600°C) and formation of corrosive by-products. Consequently, development of new precursors and processes are essential to fully explore the potential applications of ALD SnO_2 thin films.

In this work, we present a new ALD process for SnO_2 thin films with tin(IV) acetate as a novel precursor and water as a co-reactant. We studied the film deposition over a temperature range of 150-250°C. The growth rate decreased from 0.8 to 0.4 Å/cycle as the deposition temperature increased from 150 to 250 °C. All the as-deposited films were amorphous. Crystallization of the amorphous SnO_2 thin films was studied with high temperature grazing incident X-ray diffraction (HT-GIXRD) technique in air and nitrogen environments. Crystallization started at 275 °C in air, whereas in the N_2 environment it was delayed until 325 °C. In both annealing environments phase pure SnO_2 with the tetragonal cassiterite (rutile-type) structure was obtained. X-ray photoelectron spectroscopy (XPS) analysis of the as-deposited SnO_2 films confirmed that all the tin existed in the Sn^{4+} state at all the deposition temperatures. The as-deposited films exhibited a transparency of 72-87% in the visible range, with a slight decrease observed as the deposition temperature increased. Time-of-flight elastic recoil detection analysis (ToF-ERDA) indicated small amounts of carbon (~2.8 at-%) and hydrogen (~2.2 at-%) impurities in the films which decreased with the post-deposition annealing.

8:30am **AF3-TuM-3 Revealing the Effect of Defect and Hydrogenation on Borazine-based Atomic Layer Deposition using First Principles Calculations*, Tsung-Hsuan Yang,*** Tokyo Electron America*; Gyeong Hwang,* University of Texas at Austin*; Hu Li, Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Borazine ($B_3N_3H_6$) has emerged as a promising precursor for synthesizing high-quality hexagonal boron nitride (h-BN) and amorphous boron nitride (a-BN), particularly after the groundbreaking work of Hong et al. (Nature 582, 511–514 (2020)), where they claimed to grow ultralow dielectric amorphous boron nitride using chemical vapor deposition method. Leveraging its intrinsic B_3N_3 ring, borazine enables facile atomic layer deposition (ALD) without the need for additional nitrogen sources. In this work, we utilize density functional theory (DFT) to investigate the reactivity of borazine with diverse surfaces, including those with defects, hydrogen terminations, and varying degrees of hybridization (sp2 and sp3). Our findings emphasize the critical roles of surface defects and hydrogenation in governing the deposition process. Furthermore, we will discuss the self-limiting behavior observed during ALD using borazine, a key characteristic for achieving precise film thickness control.

8:45am **AF3-TuM-4 Novel Heteroleptic Precursors for Oxide Semiconductor Films (In-, Ga-, Zn-, Sn-Ox), Aimed at Co-dosing Process and Cocktail Precursor*, Nana Okada,*** *Ryota Fukushima, Keisuke Takeda, Masaki Enzu, Tomoharu Yoshino, Atsushi Yamashita, Yoshiki Oe, Akio Saito, Yutaro Aoki, Akihiro Nishida, Atsushi Sakurai,* ADEKA CORPORATION, Japan

Vertical channel transistors (VCT) with InGaZnO[1] and InGaZnTinO[2] channels deposited by ALD have been gaining attention for the 3D integration of devices, especially DRAM. A supercycle ALD with homoleptic alkyl metal precursors is commonly used: multiple metal precursors and reactants are injected step by step. It allows very controlled components, yet the process is long, and the precursors are pyrophoric[3]. Overcoming a long process, alternative approaches have been suggested such as co-dosing, which supplies multiple precursors simultaneously, and cocktail precursor, which combines precursors in one canister. However, these are challenging because all precursors must have similar volatility and mixing stability, and no precursors satisfy both requirements.

In this study, we developed new heteroleptic In, Ga, Zn, and Sn precursors: $In(Me)_2[^sBuNC(Me)C(H)C(Me)N^sBu]$ (DKI-6), $Ga(Me)_2[^sBuNC(Me)C(H)C(Me)N^sBu]$ (DKG-6), $Zn(Et)[^sBuNC(Me)C(H)C(Me)N^sBu]$ (DKZ-6), and $Sn(N^iPr_2)[^tBuNC(Me)N^tBu]$ (HTP-7) (Fig. 1). All precursors showed high volatility and non-pyrophoricity. A key feature of these materials is that they exhibit a vapor pressure difference of less than 10 °C at one torr (Fig. 2). Additionally, these materials remain stable and non-reactive when all mixed in equal moles. TGA of the mixture showed a smooth curve and no residue: 99.9% volatility (Fig. 3). ^1H NMR of the mixture had no byproduct peaks: the peaks came from each precursor (Fig. 4). Depositions of DKI-6 and DKZ-6 were done individually with H_2O on SiO_2 substrates at 150 to 300 °C. Both precursors showed ALD behavior and around 200 °C will be promising for a co-dosing and cocktail process (Fig. 5). DKI-6 and DKZ-6 at 200 °C growth rates were 0.1 and 0.2 Å/cycle respectively. X-ray photoelectron spectroscopy (XPS) indicated that impurity-free In_2O_3 and ZnO films were obtained successfully (Fig. 6). In contrast to In_2O_3, ZnO film did not have stoichiometry. This is believed to be caused by the difference in the sputtering ratio between Zn and O atoms. Moreover, DKI-6 and DKZ-6 were also reacted with O_3, and higher growth rates and impurity-free films were detected. This further investigation will be discussed at the conference.

These novel materials are promising for co-dosing and cocktail methods, offering significant process advantages like reducing flammable concerns and time consumption. The deposition of multi-component films is under investigation.

References:

1. Shosuke Fujii, Tseng Fu Lu, *et al.*, *IEDM2024*, 6-1
2. Gan Liu, *et al.*, *VLSI2024*, T16-1
3. Junghwan Kim, Jin-Seong Park, *et al.*, *ACS Appl. Mater. Interfaces* **2019**, 11, 43, 40300

9:00am **AF3-TuM-5 Investigation of Fluorinated Copper and Gold Alkoxides as Precursors for Atomic Layer Deposition*, Nick A. Hoffman,*** *David J. H. Emslie,* McMaster University, Canada

This research focuses on the development of new precursors and processes for thermal atomic layer deposition (ALD) of elemental copper and gold thin films. Most previously reported copper thermal ALD processes require deposition temperatures in the range of 100-500 °C, which can result in agglomeration and discontinuous ultra-thin films.[1] Meanwhile, there have only been three reported processes[2] for Au thermal ALD – two of these use ozone (O_3) as a co-reactant, which limits substrate compatibility, while the minimum deposition temperature for the third process using $[AuCl(PEt_3)]$ with 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine is limited by the volatility of the precursor and co-reactant. Thus, precursors which offer increased reactivity, thermal stability and volatility compared to those currently available, as well as the development of new reaction chemistries which might facilitate deposition at temperatures lower than previously reported, are of particular significance.

Herein we present a new family of fluorinated alkoxides, $[\{M(OR^F)(L)\}_n]$ (M = Cu, Au; OR^F = fluorinated alkoxide; L = PR_3, CNR), as potential precursors for thermal ALD of Cu and Au. Complexes were synthesized by straightforward and scalable methodologies, and were crystallographically and spectroscopically characterized. The thermal properties of these complexes were evaluated, displaying a wide range of thermal stability and volatility, with some precursors possessing the required characteristics for use in ALD. Solution-state reactions of these precursors with various ALD co-reactants support the thermodynamic feasibility of potential ALD reaction chemistry, yielding the target metal and volatile by-products. Select precursors were chosen for preliminary studies on a custom-built ALD reactor, leading to deposition of metallic thin films.

References

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9:15am **AF3-TuM-6 ALD of Al_2O_3 for Gas Barrier Applications: Impact of Al Precursors***, **Jean-Pierre Glauber,*** Leibniz Institute for Solid State and Materials Research, Germany*; Maximilian Gebhard, Lukas Mai,* Ruhr University Bochum, Germany*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Al_2O_3 is a versatile material system and due to its unique properties, thin films of Al_2O_3 find a range of applications in electronics, aerospace, automotive industry, anti-reflective coatings[1] packaging, gas barrier layers (GBLs)[2] etc. Especially for packaging and encapsulation of degradable goods, which are typically encapsulated by polymers such as polypropylene (PP) and polyethylene terephthalate (PET), low temperature processing of dense and amorphous Al_2O_3 thin films is required.[2] These prerequisites render atomic layer deposition (ALD) as a favorable thin film fabrication method. Trimethylaluminum (TMA) is the most commonly precursor for ALD of Al_2O_3.[3] However, the high reactivity towards moisture requires expensive safety measures and the possible formation of TMA dimers leads to difficulties in predicting and controlling the process characteristics. Combined with the lack of a defined ALD window in TMA/H_2O ALD processes, alternative Al precursors that are non-pyrophoric, but still volatile and reactive to enable low temperature ALD processes with various co-reactants including H_2O and O_2 plasma are of great interest.

We have explored [3-(dimethylamino)propyl]-dimethyl aluminum (DMAD)for PEALD of Al_2O_3 thin films on polymer substrates. The influence of the two precursors on Al_2O_3 thin film growth and film properties was investigated and compared. Thin layers of Al_2O_3 and dyads of Al_2O_3 and SiO_2 were deposited (Figure 1a) with the aim of using them as GBLs on PP substrates. Interestingly, the dyads on PP containing SiO_2 and Al_2O_3 significantly outperformed the Al_2O_3 grown with TMA in terms of barrier properties (Figure 1 b).[4]

Literature:

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9:30am **AF3-TuM-7 Atomic Layer Deposition of Nb_2O_5 using New Nb Precursor***, **Daehyeon Kim**, Suhyun Kim, Jinhyung Park,* Air Liquide, Republic of Korea

Niobium Oxides (Nb_2O_5) have been extensively utilized in various fields of technology. Traditionally these oxides have been applied as resistive films used as high-k materials for insulating layers. For instance, a thin layer of Nb_2O_5 between two ZrO_2 dielectric layers is expected to help significantly reduce leakage current and stabilize the cubic/tetragonal phases of the ZrO_2, affording higher k values in the current MIM capacitor of a DRAM. Furthermore, the application range of Nb_2O_5 expanded as HZO (HfZrO), which has ferroelectric properties, began to be applied to dielectric materials for DRAM capacitors. It is recently being studied as an interlayer between electrodes and HZO to enhance ferroelectricity of HZO.

Today, there is a growing need for a highly volatile, thermally stable, ideally low-viscosity liquid niobium precursor that allows to deposit films at high temperature in the Atomic Layer Deposition (ALD) process with a low film growth rate for precise thickness control. However, in general, thermal stability has a trade-off relationship with vapor pressure and viscosity, making it challenging to develop an ideal precursor with excellent properties across all these aspects.

To address these requirements, Air Liquide developed three Nb precursors (Nb1, Nb2, Nb3). Among them, Nb3 exhibited the most promising physical properties including not only high vapor pressure (1Torr at 105℃) and low viscosity (6.5cP at 24℃) but also high thermal stability (decomposition onset at 340℃ by DSC). It demonstrated a moderately low film growth rate of 0.4 Å/cycle, enabling precise control of film thickness. Furthermore, Nb3 showed exceptional ALD performance, achieving 100% step coverage at 350℃ and 375℃ (A/R: 1:30) and an ALD window extending up to 350℃, which is superior to the commercially available precursor in the industry.

9:45am **AF3-TuM-8 Atomic Layer Deposition of Mo Thin Film using Metal Organic Mo Precursor***, Han-Bo-Ram Lee, Bonwook Gu,* Incheon National University, Republic of Korea*; T. Barry Sean, Kieran Lawford,* Carleton University, Canada*; **Kwangyong An**,* incheon National University, Republic of Korea

The increase in integration and nanostructuring of semiconductor devices requires precisely controlled processes and improved materials properties. Molybdenum (Mo) has been actively studied as an alternative to W for the interconnects of semiconductor devices because of its low resistivity below the electron scattering regime. However, the Mo precursors reported thus far, such as $MoCl_2O_2$ and $MoCl_5$, often present challenges such as high melting points, line clogging, and particle formation. Additionally, Mo reacts easily with oxygen, making it difficult to form pure metal Mo thin films. To address these challenges, we investigated a Mo ALD process using a liquid MoCp precursor, which remains liquid at 70 °C and has a high vapor pressure of 1 Torr at 119 °C. Using hydrogen as a reactant, we successfully deposited Mo thin films at deposition temperatures below 500 °C and further improved resistivity by annealing at 950 °C for 1 hour in N_2 to reduce impurities. The lowest resistivity of the ALD Mo thin films obtained in this study was 14 μΩcm. X-ray photoelectron spectroscopy (XPS) was used to analyze the atomic concentration and bonding structure of the thin film and X-ray diffraction (XRD) was employed to evaluate its crystallinity. This study demonstrates that the MoCp precursor overcomes the limitations of conventional solid-state precursors, enhancing the reliability of Mo ALD processes. These results confirm its viability for use in advanced semiconductor technologies.

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