ALD & ALE
Room Hall 5A - Session ALDALE-MoA

Student Awardees

Moderators: Annelies Delabie, IMEC, Ivo Raaijmakers, ASM

1:30pm ALDALE-MoA-1 ALD Student Award Finalist Talk: Gas Phase Deposition of ALF-MOF for Selective CO_2 Capture: A Molecular Layer Deposition Study, *Maram Bakiro, S. Barry,* Carleton University, Canada

The synthesis of alucones, a relatively new class of hybrid inorganic-organic materials, has traditionally been achieved via molecular layer deposition (MLD) using aluminum precursors like trimethylaluminum (TMA) and alcohol-functionalized organic ligands.[1] This method allows for consecutive self limiting gas deposition of organic-inorganic hybrid films with precise control over composition and structure. Alucones are particularly noted for their inherent porosity and low density, making them suitable for applications such as ultra-low-k dielectric films.[2]

Our research presents a novel adaptation of this established process, extending the utility of the alucone deposition technique to the realm of metal-organic frameworks (**MOFs**). Addressing the need for efficient carbon dioxide (**CO_2**) capture technologies, this study presents the pioneering the MLD of aluminum formate **MOF** (**ALF-MOFs**), which is traditionally synthesized via solvothermal methods and is known for its selectively capturing CO_2.[3] Using a commercial ALD tool (Picosun R200), ALF-MOF was deposited from the gas phase through a novel process involving TMA and formic acid (H_2CO_2), **Fig 1a**.

The growth-per-cycle (GPC) was 3.5 Å for **ALF-MOF**, (**Fig 1b and c)** which is characteristic of an alucone. Mass spectrometric analysis confirmed the polymeric nature of the film, highlighting the repeat unit $Al(OOCH)_3$. Further characterization through Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy) elucidated the bridging nature of the FA ligand to the Al nodes.

Quartz crystal microbalance analysis substantiated the step-wise growth of the target **ALF-MOF**. Additionally, the exposure of **ALF-MOF** to a CO_2/N_2 gas stream demonstrated its selective CO_2 capture capabilities. This presentation will delve into the nuances of the deposition and structure of ALF-MOF, emphasizing the nature and reversibility of CO_2 uptake. Our findings represent a significant advancement in MOF deposition, showing a scalable and efficient method for CO_2 capture that could have implications for environmental sustainability and industrial applications.

(1) Vemuri, V.; King, S. W.; Lanford, W. A.; Gaskins, J. T.; Hopkins, P. E.; Van Derslice, J.; Li, H.; Strandwitz, N. C. *Chem. Mater.* **2023**, *35* (5), 1916–1925. (2) Dameron, A. A.; Seghete, D.; Burton, B. B.; Davidson, S. D.; Cavanagh, A. S.; Bertrand, J. A.; George, S. M. *Chem. Mater.* **2008**, *20* (10), 3315–3326. (3) Evans, H. A.; Mullangi, D.; Deng, Z.; Wang, Y.; Peh, S. B.; Wei, F.; Wang, J.; Brown, C. M.; Zhao, D.; Canepa, P.; et al. *Sci. Adv.* **2022**, *8*(44).

1:45pm ALDALE-MoA-2 ALD Student Award Finalist Talk: Surface Functionalization of *Poly*-Si and SiO_2 Nongrowth Surfaces with Small Inhibitor Molecules to Enable Area-Selective Atomic Layer Deposition of Al_2O_3, *Andrew Kaye,* Colorado School of Mines, USA*; H. Chandra, R. Pearlstein, X. Lei, A. Derecskei, B. Zope,* Merck KGaA*; S. Agarwal,* Colorado School of Mines, USA

Poly-Si, SiO_2, and SiN_x are three commonly used films in semiconductor manufacturing, and area-selective ALD (AS-ALD) of dielectrics on these surfaces is desirable. In this presentation, we study the reaction mechanisms of small molecule inhibitors (SMIs) with *a*-Si:H, SiO_2, and SiN_x, using *in situ* attenuated total reflection FTIR spectroscopy. On each functionalized surface, we tested the ability of SMIs to prevent the growth of Al_2O_3 from dimethyl aluminum isopropoxide and H_2O using *in situ* IR spectroscopy and *in situ* 4-wavelength ellipsometry.

On an *a*-Si:H surface, our IR data shows that aldehydes [pivaldehyde, and 3,5,5-trimethylhexanal (TMH)] chemisorb onto surface $–SiH_x$ groups to form alkoxides that are thermally stable up to ~250 °C (Fig. 1). The alkoxide formed after functionalization of *a*-Si:H with pivaldehyde is slightly more stable the alkoxide group obtained after functionalization with TMH (Fig. 1), most likely due to the absence of β hydrogen, which prevents the β-hydride elimination reaction — this limits the AS-ALD window to ~250 °C. We show that if the target growth surface is SiO_2, surface functionalization with aldehydes is selective to *a*-Si:H. If the target nongrowth surface is SiN_x, aldehydes react with surface SiH_x groups to form alkoxides. Additionally, aldehydes also react with surface $–NH_x$ groups to form of aminoalcohols,

enamines, and imines. Aminoalcohols are intermediates species and cannot be converted to imines by increasing the substrate temperature. The presence of aminoalcohols allows Al_2O_3 ALD precursors to bind to the functionalized SiN_x film, resulting in no nucleation delay.

Functionalization of SiO_2 with aminosilane SMIs has been previously reported,[1,2] but it is speculated that the presence of unreacted surface SiOH groups eventually leads to nucleation. The target growth surface in this case can be either *a*-Si:H or SiN_x. At elevated temperatures, the surface SiOH density decreases due to a H_2O condensation reaction between neighboring silicon hydroxides, leading to the formation of Si–O–Si bonds. We have studied the functionalization of SiO_2 with N,N-dimethylaminotrimethylsilane (DMATMS), which results in $–Si(CH_3)_3$ terminated surfaces. We have performed these surface functionalization experiments as a function of the pre-annealing temperature of SiO_2 to determine the optimal density of surface SiOH groups for adsorption of aminosilane SMIs (Fig. 2). Lastly, we will report the optimal surface coverage of SMIs for obtaining the highest degree of passivation for inhibiting Al_2O_3 ALD.

[1] Xu *et al.*, *Chem. Commun.* **58**, 6650 (2022)

[2] Xu *et al.*, *Langmuir* **30**, 652 (2022)

2:00pm ALDALE-MoA-3 ALE Student Award Finalist Talk: Precursor Mobility Through W Thin Films and sub-Surface Etching of Patterned TiO_2 *via* Atomic Layer Etching, *Hannah Margavio,* North Carolina State University*; N. Arellano, I. Singh, R. Wojtecki,* IBM Almaden Research Center*; G. Parsons,* North Carolina State University

Increasing complexity of nanoelectronic device architectures warrants novel atomic-scale fabrication methods. Current semiconductor processing of thin films involves distinct deposition and etch steps to achieve the desired device architecture. A key challenge, however, is to identify new process capabilities to expand synthesis of advanced materials with sub-nanometer features.[1] In this work, we describe a technique for removing thin films underneath a patterned surface in a process we term "sub-surface etching". It is known that during atomic layer etching (ALE) of thin films, a precursor converts the surface to a chemically distinct intermediate layer, and the second precursor volatilizes the conversion layer *via* ligand exchange.[2] This self-limiting mechanism assumes that: i) etching precursors remain on film surface, and ii) the entire intermediate layer undergoes volatile ligand exchange. In this work, we show that certain halogenated vapor-phase etching precursors can penetrate through thin films and react with underlying materials. To demonstrate reagent mobility through a thin film, we exposed TiO_2/Si line space patterns (shown in Figure 1a) to 10 W ALD cycles using 2% SiH_4 in Ar and WF_6 at 250 ºC. We have found that W metal deposition proceeds readily in the Si regions, and it is known that WF_6 spontaneously etches TiO_2 layers through the formation of $TiF_{4(g)}$ and $WF_2O_{2(g)}$.[2] The spontaneous etch process also leaves behind a thin layer of solid WO_xF_y on the TiO_2 surface, and we hypothesize that SiH_4 reduces the WO_xF_y layer through the formation of $SiF_{x(g)}$. A schematic of the resulting film stack is shown in Figure 1b. After 10 W ALD cycles, the resulting structure was exposed to 5 WF_6 and BCl_3 ALE cycles. The integrated 10 W ALD cycles and 5 WF_6 and BCl_3 ALE cycles deposits a 17 nm thick W layer and simultaneously etches the underlying TiO_2 feature. This process creates a uniform air gap between the etched TiO_2 and W overlayer, shown schematically in Figure 1c. We hypothesize that volatile species produced by the etch reaction diffuse out through the W overlayer. Depending on the relative WF_6 exposure, we have found the underlying TiO_2 may be partially or completely etched away. This process provides insights into the interactions between deposition and etching reaction mechanisms during integrated atomic layer process steps. More notably, this work gives a first example of vapor-phase, atomic-scale sub-surface etching and deposition, thus expanding the toolbox for thin film deposition and etching for sub-nanometer features.

[1] Clark, R. et al. *APL Mater*. **2018**, 6 (5)

[2] Lemaire, P. C.; Parsons, G. N. *Chem. Mater.* **2017**, *29* (16)

2:15pm ALDALE-MoA-4 ALD Student Award Finalist Talk: Unravelling the Role of Stoichiometry of ALD Nickel Cobalt Oxides on their Electrocatalytic Activity, *Renee van Limpt,* Eindhoven University of Technology, Netherlands*; M. Lao, M. Tsampas,* Dutch Insitute for Fundamental Energy Research (DIFFER), Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

Production of green hydrogen is a key contributor towards the development of a sustainable energy system, and the synthesis of platinum group metal-free oxygen evolution reaction (OER) electrocatalysts for H_2O

splitting is presently subject of major investigation. Nickel cobalt oxides (NCOs) have attracted particular interest[1], especially spinel NCO, since it shows excellent stable electrocatalytic performance. Rock-salt NCO, on the other hand, is also promising due to its ability to convert to the OER-active hydroxide phase. Deployment of NCO electrocatalysts requires further understanding of their chemistry-crystal structure-OER activity relationship. To this purpose, the present work focuses on ALD NCO thin film model systems which are synthesized, characterized and subjected to extended electrochemical testing.

We have recently developed an ALD supercycle process based on cobalt cyclopentadienyl ($CoCp_2$) and nickel methylcyclopentadienyl ($Ni(^{Me}Cp)_2$) precursors and an oxygen plasma co-reactant[2]. ALD provides control over the chemical composition such that the phase transition from Ni-rich rock-salt films to Co-rich spinel films can be observed at ~55 at.% Co. The transition is accompanied by an increase in the +3-to-+2 oxidation state ratio of the metal centres. Electrochemical analysis in 1M KOH discloses a synergistic effect between Co and Ni metal centres, such that NCO films are more OER-active than Co_3O_4 and NiO. The OER activity of all films is driven by the formation of (oxy)hydroxide phase. Rock-salt films continuously form hydroxide phase during CV cycling, resulting in prolonged activation such that an optimal overpotential of 470 mV is observed for the 30 at.% Co film after 500 cycles. The presence of Co limits the bulk hydroxide formation, such that a constant performance at an overpotential of ~500 mV is observed for the spinel films. The activation process occurs in parallel with an increase in the electrochemical surface area (ECSA) up to a factor 8 for rock-salt films. The overpotential is corrected for this change in ECSA upon activation using an original approach. We conclude that Ni-rich spinel films are intrinsically the most OER active[3]. The improved OER-activity of rock-salt films upon electrochemical activation indicates that the low-cobalt content films (≤40 at.% Co) could be a sustainable alternative to the more commonly investigated cobalt-rich films.

[1]Gebreslase *et al.* J. Energy Chem. 2022, 67, 101-137

[2]van Limpt *et al.* JVSTA, 2023, 41, 032407

[3]van Limpt *et al.* ACS Catal. *under review*

2:30pm ALDALE-MoA-5 ALD Student Award Finalist Talk: First-Principles Screening of Precursor Reactivity for ALD of GeAsSe Thin Films for OTS Applications, *Bram van der Linden,* KU Leuven and IMEC, Belgium*; G. Pourtois, L. Nyns, A. Delabie,* IMEC, Belgium

Storage Class Memory (SCM) with ultrahigh capacity can be realized by three-dimensional stacking of memory cells that are enclosed by wires with perpendicular alignment. Selection of one cell in these three-dimensional arrays, however, does not only lead to a voltage in the activated cell, but also in neighbouring cells. To this end, the memory cells need to be accompanied by Ovonic Threshold Switching (OTS) materials which are amorphous chalcogenides that ensure selection of the desired cell only. Atomic Layer Deposition (ALD) is essential to realize conformal OTS films on three-dimensional structures with high aspect ratios. GeAsSe is a promising OTS material, although it remains challenging to establish an ALD process with high composition control. It is therefore important to identify precursors with sufficient reactivity, which is experimentally difficult because of the many possible precursor combinations for ternary materials. We therefore employed ab initio energy calculations under the assumption of gas-phase reactions. We studied the reactivity of 13 germanium, 8 arsenic and 9 selenium precursors, amounting to more than 900 precursor combinations. Each precursor contained one of the following functional groups: alkoxy, alkyl, alkylsilyl, amine, chlorine or hydrogen.

First, successful ALD precursor combinations from the ALD AtomicLimits database and other literature were confirmed. Second, the most favourable precursor combination of all was $As(NMe_2)_3$ with $HGeCl_3$. This combination outperforms the germanium-arsenic precursor combination from literature ($AsCl_3$ with $HGeCl_3$) and both precursors show sufficient reactivity with the commonly used selenium precursor $Se(SiMe_3)_2$. Third, $Se(SnMe_3)_2$ was unreactive with most of the co-reactants and could therefore serve as a potential inhibitor for area-selective ALD. Fourth, inclusion of both hydrogen and chlorine instead of either one could help to improve the reactivity. Lastly, germanium and arsenic precursors show strikingly similar reactivity trends with the selenium co-reactants. These insights could help the precursor design for thin films that comprise GeAs, GeSe or GeAsSe.

2:45pm ALDALE-MoA-6 ALE Student Award Finalist Talk: Investigating Patterning of MgZnO by Atomic Layer Etch mode, used For Compute and Memory Applications, *Leila Ghorbani,* KU Leuven and Imec, Belgium*; S. Kundu,* IMEC, Belgium*; S. De Gendt,* KU Leuven and Imec, Belgium

Magnesium Zinc Oxide (MgZnO) emerges as a promising metal oxide for advanced memory applications due to its ability to provide thermal stability and high electron mobility > 40 cm²/VS while retaining the excellent electronic properties of pure ZnO [1]. Therefore, MgZnO finds potential applications in dynamic random-access memory (DRAM) and resistive random-access memory (RRAM) [2]. MgZnO is poised to play a crucial role in the development of electrical nanoscale devices and its patterning becomes a key challenge.

This study focuses on minimizing the chemical and physical damage occurring during the patterning process. This is crucial for preserving the carrier transport properties in these MgZnO-based thin films which in turn can impact device performance [3]. In response, we explore atomic layer etching (ALE) as a precision etching method [4] to mitigate these challenges.

The investigation involves understanding the etching mechanism in a 10 nm MgZnO film in both as-deposited state and as patterned structures using ALE mode. Initial experiments demonstrate that using Cl_2/CH_4 mixture in the adsorption step and Ar gas in the desorption step separately does not etch MgZnO. And we are able to establish an ALE window for MgZnO by combining these steps (Fig.1 a). The process reveals a controllable etching mechanism; however, the etching rate of Zn is found to be higher than that of Mg. Their respective etching mechanisms are predominantly chemical and physical for Zn, and mostly physical for Mg.

The ALE window is successfully transferred to patterned structures (pillars/spaces) with critical dimensions (CD) of 25 nm and a pitch of 90 nm. Transmission electron microscopy (TEM) (Fig.1 b) and energy-dispersive X-ray spectroscopy (EDS) results confirm minimal Mg residues between trenches and the presence of stable MgZnO composition under the hard mask (HM) used for patterning this thin layer. Half of the initial HM budget remains after etching, with reduced unwanted redeposition on the sidewalls.

This study presents a high-density demonstration of MgZnO patterning using ALE, showcasing the potential for further feature shrinkage and increased feature densities. To our knowledge, this work represents a significant achievement in the controlled patterning of MgZnO for advanced memory applications.

References

[1] Y. Li, et al. Phys. Status Solidi A, 219, (2022) 2200313.

[2] J. Hwang, et al. Materials Science and Engineering: B, 266 (2021) 115063.

[3] M. Geiger, et al. Advanced material interfaces, 7(10) (2020) 1902145.

[4] K. J. Kanarik, et al. J. Vac. Sci. Technol. A, 33(2), (2015) 020802.

3:00pm ALDALE-MoA-7 ALD Student Award Finalist Talk: In-situ FTIR Study of Oxygen Source Mixing for Hafnium Oxide Atomic Layer Deposition on Titanium Nitride, *Jin-Hyun Kim, D. Le, M. Lee, T. Chu, D. Kim, J. Veyan,* University of Texas at Dallas*; M. Benham, J. Spiegelman,* RASIRC*; S. Kim,* Kangwon University, Republic of Korea*; J. Kim,* University of Texas at Dallas

Doped hafnia is a promising material for memory applications due to its favorable ferroelectric characteristics. However, despite advanced HfO_2 ALD technology, hafnia-based ferroelectric devices continue to face challenges such as relaxation, imprint, fatigue, and breakdown.[1] Issues are linked to the interface conditions of the ferroelectric film to the electrodes. The problem worsens when the ferroelectric thickness is less than 5 nm, increasing series capacitance and hindering crystallization due to increased surface energy.[2] Therefore, enhancing the reliability and scalability of hafnia-based ferroelectrics requires understanding and optimizing the interface properties. One major source of oxygen at the oxide interface formation is the oxidation agent from the ALD process. Therefore, to minimize the formation of interfaces, the adoption of oxygen sources with a high oxidation potential is avoided. Conversely, weaker oxidants may insufficiently remove precursor ligands and other impurities, leaving contaminants that degrade the oxide film properties. This study introduces oxidant mixing as a strategy to deposit high-quality oxide films while limiting interface formation.

Employing in-situ reflectance absorption infrared spectroscopy (RAIRS), this research investigates the impact of oxidant source mixing on the surface reaction mechanism and interfacial layer. Our previous studies of HfO_2 ALD

with TEMA-Hf and H_2O, O_3, and anhydrous H_2O_2 on TiN substrate at 250°C revealed surface reactions of these oxidants.[3] O_3 exposure led to a continuous increase in Ti-O and TiN-O features, while H_2O and H_2O_2 facilitated the formation of self-limiting hydroxyl and hydroperoxyl groups on the TiN surface, effectively suppressing interfacial formation and enhancing film properties and reliability for H_2O_2-based capacitors. To investigate the effect of oxidant mixture, anhydrous H_2O_2 and a mixture with H_2O were exposed to the TDMA-Hf surface. A much milder reaction was observed using mixed H_2O_2, forming methoxy and hydroperoxyl bonds. This mild reaction indicates that surface reactivity can be controlled during ALD by adjusting the ratio of the oxygen sources. The surface reaction, material, and electrical properties of HfO_2 ALD and films deposited using mixed oxidants will be shown.

[1] J. Mohan *et al.,ACS AELM*, 4, 4 (2022).

[2] H. Lee et al., ACS AMI, 13 (2021).

[3] J. Kim et al., ALD 2023.

3:15pm ALDALE-MoA-8 ALD Student Award Finalist Talk: A New Low Temperature ALD Process for Magnesium Oxide, *Florian Preischel, D. Rogalla, A. Devi,* Ruhr University Bochum, Germany

Based on its outstanding secondary electron emission coefficient (SEEC) of up to 15 as a thin film, Magnesium (II) oxide (MgO) is emerging as an efficient SEE material for optoelectronic applications.[1,2] Additionally, the non-toxicity and biocompatibility of MgO[3,4] enable its use as a protective gas-barrier layer on food packaging, for the encapsulation of pharmaceuticals and owing to its antibacterial properties it also appealing for the coating of medical implants.[5]

To transition these applications from research to industrial applications, it is necessary to develop scalable processes that enable the deposition of high-quality, defect-free MgO films. Specifically, SEE layers and the coating of (heat-)sensitive substrates necessitate mild, low-energy coating methods.[2,6,7] Owing to its self-limiting nature, ALD emerges as the most promising solution that offers a precise control over the thickness and morphology. Yet, ALD strongly relies on the underlying chemistry and the development of low-temperature thermal processes for MgO is currently restricted by the availability of suitable Mg precursors. Existing precursors are limited to compounds of the cyclopentadiene and β-diketonate type that require elevated temperatures or harsh co-reactants.[8,9]

Addressing this challenge, we herein introduce bis-(dimethylamino)propyl magnesium (II), [Mg(DMP)$_2$] that was designed to be thermally stable, yet highly volatile and reactive to facilitate low-temperature thermal ALD of MgO. The thermal properties of [Mg(DMP)$_2$] were evaluated by thermogravimetric analysis (TGA), revealing a high volatility and indicating its potential as an ALD precursor for MgO. Subsequentially, we developed a thermal ALD process for MgO with [Mg(DMP)$_2$] and water in a broad temperature range from 40 °C to 260 °C on Si substrates. ALD characteristics of saturation and linear growth were demonstrated with high GPC values of 1.91 Å at 120 °C and 2.40 Å at 40 °C (**Figure 1**, left), indicative for efficient surface reactions. The purity and stoichiometry of the resulting films, confirmed by RBS/NRA (**Figure 1**, right), underlines the potential of this approach for emerging MgO applications. By identifying a new and promising Mg precursor and an ALD process that can operate close to room temperature, including coating on polymer substrates, we advance the utilization of MgO thin films for new applications based on its unique properties.

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