ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-TuA
Novel ALD Processing

Moderators: Agnieszka Kurek, Oxford Instruments Plasma Technology, Netherlands, Dr. Matthias Minjauw, Ghent University, Belgium

4:00pm **AF2-TuA-11 Electron-Enhanced ALD and CVD at Low Temperature Using Reactive Background Gas***, Z. Sobell, S. George,* ***Andrew S. Cavanagh,*** University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiN, TiO_2, and TiCN films at T < 70 °C. EE-ALD was employed with a reactive background gas (RBG) present concurrently during the EE-ALD process (Figure 1). Three Ti-based films were all grown using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) precursor and electrons together with the continuous presence of RBG. The three RBGs utilized to tune the film composition were ammonia (NH_3), oxygen (O_2), and methane (CH_4).

TiN EE-ALD was performed at T < 70°C using TDMAT together with an NH_3 RBG at a pressure of ~1 mTorr. NH_3 is believed to interact with the electron beam and liberate •H and •NH_x radicals. The •NH_x radicals may facilitate Ti nitridation and C removal from the film. The TiN films nucleated rapidly and displayed purities of > 96% and ultralow resistivities of < 120 µΩ-cm. These films may be useful as diffusion barriers in backend interconnects.

TiO_2 EE-ALD was performed at T < 70 °C using TDMAT together with an O_2 RBG at ~1 mTorr. O_2 is believed to interact with the low energy electron beam, creating •O radicals which add oxygen to form TiO_2 and remove any N and C from the TDMAT precursor. XPS showed no detectable C or N in the TiO_2 films and a slightly O-rich stoichiometry. Oxygen-rich TiO_2 films may be more photochemically active due to bandgap narrowing and may be useful in photocatalysis. TiCN EE-ALD was also deposited at T < 70 °C using TDMAT together with a CH_4 RBG at a pressure of ~0.2 mTorr. The TiCN films were C-rich, with a stoichiometry of $Ti_{1.6}N_1C_{4.3}$ as measured by XPS after surface sputtering. TiCN is a promising amorphous diffusion barrier for back-end interconnects.

Electron-Enhanced chemical vapor deposition (EE-CVD) was also used to deposit WN and SiC films at T < 100 °C. EE-CVD films were grown by pulsing the precursor with the electrons and RBG present continuously during the deposition (Figure 2). EE-CVD offers enhanced growth rates for some systems compared with EE-ALD. WN EE-CVD was performed at T< 100 °C using $W(CO)_6$ with NH_3 RBG present at a pressure of ~1 mTorr. The WN films were free from C and O by XPS after surface sputtering. The WN EE-CVD films also displayed a low resistivity of 468 µΩ-cm as measured by spectroscopic ellipsometry. In addition, SiC EE-CVD was demonstrated at T < 100 °C using Si_2H_6 with CH_4 RBG present at a pressure of ~0.45 mTorr. The SiC films were stoichiometric as measured by XPS after surface sputtering with a small (<3%) oxygen signal likely from atmospheric oxidation.

4:15pm **AF2-TuA-12 ALD of Multicomponent Films Using Precursor Co-Dosing***,* ***Paul Poodt,*** Eindhoven University of Technology, The Netherlands

A growing number of ALD applications require the deposition of ternary or quarternary compounds. Examples include doped films (e.g. ZnO:Al), mixed oxides to tune dielectric properties (e.g. HfZrO), tunable bandgap materials for solar cells (e.g. ZnOS-) or opto-electronic materials (e.g. InGaN), and high mobility oxide semiconductors (e.g. InGaZnO). A common method to deposit multicomponent films in ALD is the supercycle approach [1], where sub-cycles of different binary compounds are combined to deposit films where the resulting net composition is determined by the cycle ratio of the individual sub-cycles. A drawback of the supercycle method is that essentially multilayer stacks are deposited instead of true alloys and the film composition varies out-of-plane, potentially impacting film properties.

An alternative method is to use precursor co-dosing, where two or more precursors are simultaneously dosed and co-adsorb during a half-reaction. The resulting film composition is then determined by the ratio of the partial pressures of the individual precursors during the precursor dose. As each ALD cycle deposits a true alloy, it results in excellent out-of-plane compositional uniformity. The co-dosing method has first been reported in the late 1980's to deposit ternary and quarternary III-V compounds [2] and has been used since for a wide range of materials. In the last decade it has become the method of choice for depositing multicomponent materials with Spatial ALD.

A proper understanding of the relation between film composition and precursor partial pressure during co-dosing is essential for accurate control of the film composition. This is not straightforward, as the surface chemistry of co-dosing can be quite complex, involving competitive adsorption, heterogeneity of reactive sites, exchange reactions and more. We willdiscuss how the surface chemistry of precursor co-dosing determines the film composition. In analogy to the IUPAC classification of adsorption isotherms for single adsorbents [3], we will introduce a similar classification of adsorption isotherms for multiple absorbing precursors which we will use to review and explain results reported in literature. Finally, we will discuss some interesting new opportunities for co-dosing, such as the deposition of gradient composition films and the use of co-dosing for area-selective deposition.

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[2]: M. Tischler, S. Bedair, J. Cryst. Growth 77 (1986) 89

[3]: M. Thommes et al, Pure & Appl. Chem. 87 (2015) 87

4:30pm **AF2-TuA-13 Controlling the Nucleation and Growth in Atomic Layer Deposition of Ruthenium: The Role of Surface Diffusion***,* ***Amnon Rothman****, A. Werbrouck, S. Bent,* Stanford University

Atomic layer deposition (ALD) of noble metals has gained significant attention due to its potential uses in areas such as microelectronics, catalysis, and nanotechnology applications. Ruthenium is an attractive noble metal due to its beneficial physical properties, including low bulk resistivity and high work function, making it suitable for catalysis and integrated-circuit applications such as capacitor electrodes for dynamic random-access memories (DRAM). However, due to an island growth mechanism and nanoparticle formation, forming continuous and pinhole-free layers from Ru metal ALD on oxide surfaces can be difficult, leading to poor-quality films. These nonidealities are mainly due to the poor wettability of these low-surface energy surfaces and the lack of nucleation sites on the oxide substrate. In order to maximize the potential of ALD, it is important to fully understand the nucleation and growth mechanism of the ALD process and to develop ways by which nucleation can be enhanced.

In this work, we study the nucleation enhancement of ALD ruthenium layers on silicon substrates by using single organometallic monolayers, with and without H_2O exposure, prior to deposition. The resulting nucleation and growth mechanism is studied using scanning electron microscopy (SEM), ellipsometry, and X-ray photoelectron spectroscopy (XPS) on the treated and untreated substrates. Ru ALD nucleation enhancement is observed after the different types of pre-treatments. Unlike previous studies that relate the enhancement mechanism to a ligand exchange reaction between the chemisorbed organometallic molecules and the gaseous metal precursor, the current study relates the enhancement to other atomistic processes such as surface-diffusion of adatom and nanoparticle nucleation, diffusion, and coalescence. A model based on the Avrami nucleation and growth equation is fitted to the experimental results, pointing to the possible growth enhancement mechanism, which we hypothesize to be an increase in the surface diffusivity of nanoparticles/adatoms on the pretreated surface. Understanding the enhancement mechanism by pretreatment with organometallic molecules introduces a potential route to achieve improved nucleation and growth of ultrathin films.

4:45pm **AF2-TuA-14 Combining Atomic Layer Deposition Routes and Solvothermal Conversion: Towards Access to Layer Stacking of Porphyrin-Based Mofs***, B. Gikonyo,* ***Catherine Marichy****, S. Forel, A. Fateeva,* Laboratoire des Multimatériaux et Interfaces, CNRS/Université Claude Bernard Lyon 1, France

Metal-organic frameworks (MOFs) have received much attention as promising porous materials with wide range of applications, such as gas storage or separation, catalysis, drug delivery, or electrochemistry. In the latter field, porphyrin-based MOFs are attractive as for fuel cells, and electrocatalysis.[1] For real breakthroughs, fine-tuning of their structure and thus physico-chemical properties with high precision is required. In particular, incorporating metals into the tetrapyrrolic core has proven effective to impart new functionality such as optical properties and electrocatalytic activity. Besides, to integrate these hybrid materials into microelectronic devices, thin films are needed. In these regards, atomic layer deposition (ALD) based approaches are highly promising. Combining ALD of metal oxide with its solvothermal conversion into MOF has proven to be an efficient route that allows fabricating MOF layers on various substrates.[2,3] Furthermore, vapor phase infiltration (VPI) is an elegant post-synthesis modification path for tuning MOF properties while preserving the network structure. VPI has been demonstrated enabling the insertion of

metal cation into mesoporous and microporous MOFs.[4,5,6] Herein, ALD and VPI along with solution-based synthesis are implemented to fabricate functionalized porphyrin-based MOF films on FTO and Si substrates. Particular attention is given to the fabrication of layer stacking of MOFs. Briefly, Al-PMOF[7] thin films are first fabricated by the solvothermal conversion of an ALD grown Al_2O_3 seed layer, as previously reported.[2] Then, using a single precursor, isolated metallic entities are installed by VPI in the porphyrinic core, modifying the optical properties of the MOF thin film. A second metal oxide deposition and conversion step leads to a stacking of porphyrinic MOF films with different composition and optical properties. The obtained Al-PMOF, modified-Al PMOF layers and bilayers are characterized in terms of morphology, composition, structure and optical properties. In particular, UV-Visible and photoluminescence spectroscopies permit monitoring the different fabrication steps. By adjusting the ligand and the metal inserted into the MOF core, tunable stacking of various porphyrin-based MOFs is expected accessible.

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5:00pm **AF2-TuA-15 Crystal Phase Transition of Atomic Layer Deposited Antimony Telluride Thin Films with Thickness and Substrate-Dependent Orientations**, ***Sangyoon Lee**, J. Seo, I. Sohn,* Yonsei University, Korea*; Y. Kang, C. Lee, W. Yang,* Samsung Advanced Institute of Technology, Republic of Korea*; S. Chung, H. Kim,* Yonsei University, Korea

With the advances for the vertical-NAND flash memories, phase-change memory (PCM) has attracted enormous interests as one of the next-generation storage-class memory, combined with ALD technologies.[1] In general, the PCMs are composed of complex chalcogenide alloys which can be tuned by ternary or quaternary alloys such as Ge-Sb-Te (GST).[2] Among chalcogenides for PCMs, antimony telluride (Sb_2Te_3) has been considered as a candidate with a high crystallization speed. While it is the basic component of the GST, Sb_2Te_3 has received relatively less attention due to its low thermal stability and electrical resistivity. However, in recent years, the stacking and forming heterostructures composed of chalcogenides including Sb_2Te_3 has been found to have huge potential as PCM.[3] Since the out-of-plane orientations of heterostructured layers is important, the atomic-scale observation of film growth and crystallinity formation of Sb_2Te_3 is required, including substrate dependency. Though, most of studies have focused on the formation of GST alloys, not the growth of ALD Sb_2Te_3 itself. Herein, we aimed to investigate the atomic-scale thin film growth and phase transition of ALD Sb_2Te_3 thin films. Comparatively, thin film growth modes of ALD Sb_2Te_3 on amorphous and crystalline substrates were studied by observing transformation of crystal structures. On SiO_2, predominant amorphous phases at initial growth stage were observed, followed by polycrystalline island growth with randomly oriented grains. However, on crystalline W, the highly out-of-plane (00l) orientations and layer-by-layer growth was found. Furthermore, the consequent changes in electrical resistivity of ALD Sb_2Te_3 were observed to examine the correlations with substrate-dependent film orientations. We anticipate that this work can contribute to understanding of atomic-scale growth of ALD Sb_2Te_3 thin films, which will be utilized in a wide range of applications.

Acknowledgement

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5:15pm **AF2-TuA-16 Molecular Layer Deposition as a Strategy to Direct Polymer Adsorption and Crystallization**, ***Maurice Brogly**, S. Bistac, D. Bindel,* Université de Haute Alsace, France

Deposition of dedicated organic molecules on a substrate appears as an efficient strategy to control its surface properties of the substrate such as wettability or surface reactivity. These modified surfaces have many applications in polymer coatings, hybrid or composite materials as they contribute to improve polymer adsorption and adhesion onto the modified substrate. Thiol or silane based organic molecules are good candidate as they self-assemble after deposition from solution. An understanding of the mechanisms governing the growth and structure of this thin organic layer is a major step forward for optimal performance of the resulting coating, hybrid or composite material. This study focuses on the adsorption and grafting from solution of such self-assembling monolayer (SAM) on various substrates (Au, Al). Main objectives are to understand how SAM molecules absorb and bond to metallic substrates, how they organize to form SAM, and how their tail functional group direct polymer adsorption and crystallization. The characterization techniques used were wettability to access surface energy of the substrates before and after grafting, atomic force microscopy (AFM) to characterize the morphology of the organic thin layer formed, and polarization modulation infrared spectroscopy in reflection mode (PM-IRRAS) to access the molecular orientation of the adsorbed molecules. This study contributes first to understand the mechanisms that govern adsorption, growth, and structuration of these molecular layer on metal substrates. As an example, it's shown that the tilt angle of the grafted molecule depends on the nature of the substrate, but mainly on the nature of the anchoring group functionalities. In a second step homopolymers and copolymers were spin-coated on these modified metal substrates. The influence of the surface chemistry of the substrate on the organization and structuration of homopolymers and copolymers of different compositions was then studied. Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between polymer/polymer and polymer/substrate interactions, which will have a direct effect on the crystallization. This was explained by changes in the balance of polymer/polymer vs polymer/substrate interactions as the surface chemistry of the substrate drives the balance between these interactions.

Reference : M. Brogly & al, Applied Surface Science, 2022, 603, 154428

5:30pm **AF2-TuA-17 Optical Monitoring of $MoCl_5$ Delivery for Atomic Layer Deposition Applications**, ***Berc Kalanyan**, E. Jahrman, J. Maslar,* National Institute of Standards and Technology

Vapor phase deposition of molybdenum films using fluorine-free precursors is desirable for fabrication of interconnects in transistor and flash memory structures. ALD is well-suited to this task due to its low thermal budget and high conformality, enabling its integration into back-end processing. The reduction of molybdenum pentachloride ($MoCl_5$) with hydrogen is one of several known methods to deposit metallic Mo films[1,2]. While $MoCl_5$ is attractive for deposition applications, it is a low-volatility solid under typical delivery conditions and readily forms volatile oxychlorides upon exposure to trace moisture. The challenges associated with achieving sufficient $MoCl_5$ flux are reflected in the literature by a wide range of vessel temperatures used for nominally the same deposition chemistry (e.g., 70 °C to 210 °C for MoS_2 ALD[3,4]). Further, the potential existence of oxychlorides in the vapor phase is problematic because those species are reactive toward surfaces and can serve as precursors for film deposition[2,5]. An additional complexity is the tendency of $MoCl_5$ to etch Mo and Mo-containing films[6]. Therefore, a detailed understanding of $MoCl_5$ deposition behavior requires *in situ* measurement of the partial pressures of $MoCl_5$ and reactive impurities such as $MoOCl_4$.

To address this need, we employed direct absorption measurements to monitor the partial pressure and delivery rates of $MoCl_5$ as a function of operating conditions typical for ALD. We first measured quantitative vapor phase spectra of neat $MoCl_5$, $MoOCl_4$, and MoO_2Cl_2 using an ultraviolet-visible (UV-vis) spectrometer under static conditions. We evaluated the stability of the compounds in the optical cell and in the ampoule headspace using a large number of replicate measurements and peak fitting. We used spectral fingerprints for $MoCl_5$ and $MoOCl_4$ to design in-line non-dispersive gas analyzers with selectivity toward each species. Gas analyzers consisted of a broadband source, filters for wavelength selection, and avalanche photodiodes. Using results from these measurements, we will present on the reproducibility of $MoCl_5$ delivery rates, sensitivity to $MoOCl_4$ contamination, and precursor aging. Potential implications for deposition applications will also be discussed.

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Author Index

Bold page numbers indicate presenter

— B —
Bent, S.: AF2-TuA-13, 1
Bindel, D.: AF2-TuA-16, 2
Bistac, S.: AF2-TuA-16, 2
Brogly, M.: AF2-TuA-16, **2**
— C —
Cavanagh, A.: AF2-TuA-11, **1**
Chung, S.: AF2-TuA-15, 2
— F —
Fateeva, A.: AF2-TuA-14, 1
Forel, S.: AF2-TuA-14, 1
— G —
George, S.: AF2-TuA-11, 1
Gikonyo, B.: AF2-TuA-14, 1
— J —
Jahrman, E.: AF2-TuA-17, 2
— K —
Kalanyan, B.: AF2-TuA-17, **2**
Kang, Y.: AF2-TuA-15, 2
Kim, H.: AF2-TuA-15, 2
— L —
Lee, C.: AF2-TuA-15, 2
Lee, S.: AF2-TuA-15, **2**
— M —
Marichy, C.: AF2-TuA-14, **1**
Maslar, J.: AF2-TuA-17, 2
— P —
Poodt, P.: AF2-TuA-12, **1**
— R —
Rothman, A.: AF2-TuA-13, **1**
— S —
Seo, J.: AF2-TuA-15, 2
Sobell, Z.: AF2-TuA-11, 1
Sohn, I.: AF2-TuA-15, 2
— W —
Werbrouck, A.: AF2-TuA-13, 1
— Y —
Yang, W.: AF2-TuA-15, 2