ALD Fundamentals
Room Grand Ballroom A-G - Session AF-MoA
Precursors and Processes

Moderators: Prof. Seán Barry, Carleton University, Dr. Scott Clendenning, Intel Corporation

4:00pm **AF-MoA-11 Precursors for Photoassisted Area Selective Deposition on Self Assembled Monolayers***, B. Das, R. Singh, C. Brewer,* University of Florida*; R. Holliday, A. Walker,* University of Texas at Dallas*; **Lisa McElwee-White**,* University of Florida **INVITED**

Photoassisted chemical vapor deposition (PACVD), or photochemical CVD, is a technique that can be used for metallization of thermally sensitive substrates such as patterned self-assembled monolayers (SAMs), providing a potential route to area selective deposition (ASD) through different reactivity with the terminal functional groups of the SAM.In this project, photochemical dissociation of the precursor occurs in the gas phase and is dependent upon the photochemical and subsequent thermal reactivity of the precursor.The reactivity is controlled by the excited state properties and bond dissociation energies of the precursor and can be assessed by determining quantum yields for starting material disappearance and appearance of ligand loss products. Screening for the decomposition efficiency of potential precursors for PACVD can be used in a downselection process before deposition experiments begin.

Readily available Ru and Mn compounds, including (η^3-allyl)Ru(CO)$_3$X, (η^4-diene)Ru(CO)$_3$ and RMn(CO)$_5$ complexes, have been assessed for their potential use in ASD by PACVD.Precursor design, electronic structure, and photochemical reactivity of the complexes will be discussed in the context of the results of PACVD of Ru or Mn on functionalized SAMs.

4:30pm **AF-MoA-13 Reductive Thermal ALD of Pd and Au Thin Films***, **Anton Vihervaara**, T. Hatanpää, H. Nieminen, K. Mizohata, M. Chundak, M. Ritala,* University of Helsinki, Finland

Gold and palladium thin films have many potential applications in microelectronics, protective coatings, catalysis and MEMS. Many ALD processes, especially for noble metals, are either highly oxidative or plasma enhanced. While these approaches to the deposition of metal thin films do have their advantages, they also impose challenges. Thus, reductive thermal processes are needed as alternatives. 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine[1] and 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine[2] ((Me$_3$Si)$_2$DHP and (Me$_3$Ge)$_2$DHP) are both relatively novel reducing agents with only few reported ALD processes. In our recent research, we developed a low temperature ALD process for nickel using NiCl$_2$(PEt$_3$)$_2$ and (Me$_3$Ge)$_2$DHP.

In this study, ALD of gold[3] and palladium was realized by combining AuCl(PEt$_3$)with (Me$_3$Ge)$_2$DHP, and PdCl$_2$(PEt$_3$)$_2$with (Me$_3$Si)$_2$DHP. High purity gold films were successfully deposited at 180 °C. Metallic palladium was also deposited at the same temperature. ALD characteristics were confirmed and saturative growth achieved with these processes. While the gold films were extremely pure having less than 0.5 at.% of impurities, Pd films had significantly more of carbon and phosphorus (14 and 5 at.%, respectively). This is likely caused by decomposition of the PEt$_3$ ligands, catalyzed by the Pd surface. However, since neither film had any chlorine, we can conclude efficient reduction of the metal ions. The resistivities of the films correlated with the impurity contents. The gold films had resistivities very close to the bulk value, while the Pd films had much higher resistivities. The gold process had a growth rate of 1.7 Å/cycle, while for the Pd it was 0.4 Å/cycle. When PdCl$_2$(PEt$_3$)$_2$ and (Me$_3$Ge)$_2$DHP were combined, surprisingly, PdGe$_x$ films were obtained.

Based on these and our earlier experiments, we have successfully extended the combination of volatile metal chloride precursors and DHP-type reducing agents, originally demonstrated with (Me$_3$Si)$_2$DHP by prof. Winter and co-workers, as an avenue for reductive, oxygen-free thermal ALD of metals. We have also established the applicability of AuCl(PEt$_3$)and PdCl$_2$(PEt$_3$)$_2$ in ALD processes, both being valuable additions to the slim library of proper ALD precursors for these metals.

(1) Klesko, J. P. et al. *Chem. Mater.***2015**, *27* (14), 4918–4921. https://doi.org/10.1021/acs.chemmater.5b01707.

(2) Vihervaara, A. et al. *Dalt. Trans.***2022**, *51* (29), 10898–10908. https://doi.org/10.1039/D2DT01347A.

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

4:45pm **AF-MoA-14 Phosphorus Zintl Species as ALD precursors for Metal Phosphide Thin Films***, **Paul Ragogna**, J. Bentley,* Western University, Canada*; E. Goodwin,* Carleton University, Canada*; J. Lomax,* Western University, Canada*; B. Van Ijzendoorn, M. Mehta,* University of Manchester, UK*; S. Barry,* Carleton University, Canada

Atomic Layer Deposition (ALD) is a thin film deposition technique in which precursors sequentially saturate a substrate surface in a self-limiting reaction. This nanoscale process enables the tuning of instrument parameters to synthesize thin films of controlled thickness which results in varied physical and electronic material properties.[1] Metal phosphide thin films can be prepared by vapour deposition techniques using various combinations of metal and phosphorus precursors, and these materials have applications in microelectronics, catalysis, and energy storage.[2,3] Group 13 and 14 materials such as GaP, InP, and GeP possess bandgaps that are amenable to photovoltaic and transistor applications and are derived from PH$_3$, an extremely toxic and pyrophoric reagent requiring specialized facilities. [4] Heptaphosphide (P_7^{3-}) is a relatively easy to prepare Zintl species with various binding modes possible with an electron-deficient metal,[5] and given its structural difference from PH$_3$, a diverse series of metal phosphide film compositions can be produced. In this context, the thermal properties and utility of P$_7$(SiMe$_3$)$_3$ as a phosphorus precursor combined with Group 13 species to produce metal phosphide films were investigated. The P$_7$(SiMe$_3$)$_3$ cluster is sufficiently robust up to ~250 ºC (by DSC) and the precursor also has virtually no residual mass as measured by TGA, and an extrapolated volatilization temperature at 1 torr (T_v) of ~130 ºC. The volatilization and saturative behaviour of the precursor was analyzed by QCM which demonstrated saturation of an Al$_2$O$_3$ crystal to ~16.32 ng/cm^2. As an example of the applicability of P$_7$(SiMe$_3$)$_3$, an ALD processes was performed with P$_7$(SiMe$_3$)$_3$ and AlMe$_3$ with the investigation of other secondary precursors currently on-going. The resulting materials were investigated using quartz crystal microbalance, XPS, ToF-SIMS, AFM and SEM.

[1]Miikkulainen, V. *et al. J Appl. Phys.* **2013**, 113, 021301; [2] Shi, Y. *et al. Chem. Soc. Rev.*, **2016**, *45*(6), 1529–1541; [3] Callejas, J. F. *et al. Chem. Mat.*, **2016**, *28*(17), 6017–6044;[4] Lu. Y. *et al. RSC Adv.*, **2016**, 6, 87188; [5] Turbervill, R. S. P. *et al*. *Chem. Rev.*, **2014**, *114*(21), 10807–10828.

5:00pm **AF-MoA-15 Investigation of Discrete Reactant Feeding for Atomic Layer Deposition of In$_2$O$_3$ Using Novel Liquid Alkyl-Cyclopentadienyl Indium Precursor***, **Hae Lin Yang**, H. Kim,* Hanyang University, Republic of Korea*; T. ONO, S. KAMIMURA, A. EIZAWA, T. TERAMOTO, C. DUSSARRAT,* Air Liquide Laboratories, Japan*; J. Park,* Hanyang University, Republic of Korea

An interest in indium oxide (In$_2$O$_3$)-based metal oxide semiconductors, such as In$_2$O$_3$, indium-gallium oxide (IGO), indium-zinc oxide (IZO), and indium-gallium-zinc oxide (IGZO) for the use of electronic devices has been increased. In particular, In$_2$O$_3$ is spotlighted as a material capable of controlling oxygen vacancies and impurity concentrations to achieve higher carrier mobility[1]. Therefore, an investigation for a novel indium precursor for ALD which is able to obtain a wide process window, superior growth rate, uniformity, and film quality has increased. Nowadays, In$_2$O$_3$ film deposition using metal-organic precursors has been fully investigated but the process of high-temperature region, over 300℃, is not much reported due to the thermal stability. Although the precursors that have cyclopentadienyl (Cp) functional groupare reported stably react over 300℃,[2] InCp is not favorable in the industry because it is a solid phase at room temperature which leads to a particle issue during the process and reported co-oxidant, H$_2$O and O$_2$ plasma show poor conformality on the complex structure. For this reason, our group has evaluated the novel indium alkyl cyclopentadienyl, which has high stability, a broad process window (200-400℃), and a liquid phase at room temperature. In this study, not only the introduction of a new precursor but also the development of the deposition process to obtain an order of double higher growth rate than the conventional method. We adopted a discrete reactant feeding (DRF) to improve the growth rate in this study. This optimized ALD process shows a very high growth rate of 2.0Å/cycle and negligibly low residual carbon impurities around the XPS detection limit. Also, a very wide process temperature range (200-400℃) was obtained and various film analysis methods such as XPS, XRR, XRD, and AFM are used to evaluate the In$_2$O$_3$ film quality. Therefore, the indium precursor having alkyl cyclopentadienyl derivative is one of the promising candidate precursors to form a high-quality In$_2$O$_3$ film for use in the future semiconductor field.

5:15pm **AF-MoA-16 Synthesis and Precursor Property Evaluation of Er Enaminolate Complexes and Deposition of Er_2O_3 Thin Film using Thermal Atomic Layer Deposition (ALD)***, **Chamod Dharmadasa**, C. Winter, N. Jayakodiarachchi,* Wayne State University*; P. Evans,* University of Wisconsin-Madison*; R. Liu,* University of Wisconsin - Madison

Lanthanide oxide films have many applications in optics, catalysis, and semiconductor devices. Er_2O_3 films have useful properties that arise from its high dielectric constant, a large band gap energy, high refractive index, and thermodynamic stability at high temperatures. These properties have led to the investigation of Er_2O_3 films for possible inclusion in CMOS devices, antireflective and protective coatings on solar cells, and passivation layers for III-V semiconductors. Er_2O_3 films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique since it gives Angstrom-level thickness control and can afford 100% conformal coverage in high aspect ratio features. ALD precursors reported to date for Er_2O_3 films have problems that include low reactivity toward water as a co-reactant, oxidation of substrates when ozone is used as the co-reactant, and variable thermal stabilities. Recently, we described a series of volatile and thermally stable lanthanide(III) complexes that contain enaminolate ligands.[1] We report here detailed synthetic studies of the $Er(L^1)_3$ precursor complex, its ALD precursor properties, and its use in the ALD of Er_2O_3 films using water as the co-reactant. Depending upon the reaction conditions during precursor synthesis the compounds $Er(L^1)_3$, $Er(L^1)_3(L^1H)$, or $K[Er(L^1)_4]$ can be isolated. The reaction conditions can be selected to provide high yields of $Er(L^1)_3$. The volatility and thermal stability characteristics of $Er(L^1)_3$ are favorable for use as precursors for Er_2O_3 and other rare-earth oxides. An ALD window in the growth of Er_2O_3 films using $Er(L^1)_3$ with water as the co-reactant was observed from 150 to 250 °C, with a growth rate of 0.25 Å/cycle. The films were characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy. Advantages of $Er(L^1)_3$ include its simple synthesis, good volatility and high thermal stability, and high reactivity with water to afford Er_2O_3 films. This class of new ALD precursors has the potential to enable more widespread use of the favorable properties of rare-earth oxide compounds and can be expanded to multi-component complex oxides containing rare earths.

1. N. Jayakodiarachchi, P. G. Evans, C. L. Ward, C. H. Winter, *Organometallics***2021**, *40*, 1270-1283.

5:30pm **AF-MoA-17 Deposition of $CsSnI_3$ Perovskite Thin Films by Atomic Layer Deposition and Pulsed Chemical Vapor Deposition***, **Alexander Weiß**, M. Terletskaia, G. Popov, M. Leskelä, M. Ritala, M. Kemell,* University of Helsinki, Finland

Cesium tin triiodide ($CsSnI_3$) belongs to the group of halide perovskites, materials with outstanding optoelectronic properties. Halide perovskites gained huge interest in the past decade because they can be used as thin film solar absorbers in perovskite solar cells. This young technology has the potential to deliver low-cost solar energy and has already reached promising power conversion efficiencies above 25 %.

$CsSnI_3$ exhibits a small band gap energy (1.2 – 1.3 eV) and is Pb-free, providing a lower toxicity compared to its Pb-containing analogues, such as $CH_3NH_3PbI_3$ (MAPI) or $CsPbI_3$. Therefore, it is an attractive candidate for an environmentally friendlier and less hazardous absorber layer for perovskite solar cells.

Before perovskite solar cells can become widely commercially available, two problems need to be solved: The lacking scalability to large and/or complex-shaped areas, and the instability impeding the durability of the solar cell. We aim to tackle the scalability issue by employing Atomic Layer Deposition (ALD) as the key method. We believe that developing an ALD-based process for $CsSnI_3$ can also address the stability issue of the perovskite layer. Inorganic perovskites, especially solid-solution perovskites, are reportedly more stable than their organic-inorganic hybrid analogues. Combining an ALD-based $CsSnI_3$ process with our earlier $CsPbI_3$ ALD process[1] or our ALD-based MAPI process[2] would enable the scalable deposition of such solid-solution halide perovskites.

In this work, we report two new ALD-based routes to deposit $CsSnI_3$ thin films. The first route relies on a two-step approach, starting with the deposition of ALD CsI[1] that is subsequently exposed to a new ALD SnI_2 process to convert it to $CsSnI_3$. The ALD SnI_2 process uses $Sn(btsa)_2$ (btsa: bis(trimethylsilyl)amide) and SnI_4 as precursors, works in a narrow temperature range (75 – 90 °C) on CsI and yields phase-pure γ-$CsSnI_3$ films. The second route relies also on the deposition of ALD CsI but in this case it is converted to γ-$CsSnI_3$ by pulsed Chemical Vapor Deposition (pCVD) of SnI_2 using the same precursors. This process works at similar temperatures (160 – 180 °C) as the ALD CsI process, therefore effectively making it a one-step approach that is much faster than the first route. Moreover, exposing the CsI film to the pCVD SnI_2 process at these elevated temperatures ensures that the excess SnI_2 is sublimed, making this process self-limiting with respect of the ternary film composition.

[1] A. Weiß et al., *Chem. Mater.* **2022**, 34, 13, 6087–6097

[2] G. Popov et al., *Chem. Mater.* **2019**, 31, 3, 1101–1109

ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF-MoP
ALD Fundamentals Poster Session

AF-MoP-2 Atomic Layer Deposition of hfo2 Thin Film Using a Novel Heteroleptic Ethylenediamine Based Hf Precursor*, **Choel Wan Park**, E. Shin, E. Cho, H. Kim, K. Mun, K. Lee, J. Park,* Hansol Chemical Co., Ltd., Republic of Korea

Group 4 metal oxide materials such as ZrO_2, TiO_2, and HfO_2 have attracted considerable attention for dielectric materials for microelectronic devices. HfO2 film has an outstanding high-dielectric constant (κ ~ 20-25, t-HfO2) , large band gap Energy (E_g, ~ 6.0 ev) and good thermal stability. For these reason, the HfO_2 thin film applicate microelectronic devices such as the dynamic random access memory (DRAM) capacitors and central processing memory (CPU) gate dielectric application.

In this study, we propose a novel heteroleptic ethylendiamine based Hf precursor namely HEA. The physical characteristic of HEA was investigated by NMR Spectroscopy. Also, we measure the properties of the HfO_2 thin film of HEA against usually usedCpTDMAH by thermal atomic layer deposition (TALD).

The evaporation characteristics of HEA and CpTDMAH were carried out in a thermogravimetric analysis (TGA). The amount of residue was about < 0.45 % for HEA, which had a less residue compared to CpTDMAH (< 0.98 %). For both precursors HEA and CpTDMAH, the characteristic self-limiting ALD growth mode was confirmed. The growth rate of HEA was 1.19 Å/cycle with ozone as a reactant gas and showed a Low temperature ALD window in a range of 150–250°C.

HfO_2 thin film properties were investigated by SIMS depth profile and Transmission electron microscope (TEM). The deposited film of HEA represented better step coverage and improved carbon impurity compared to that of CpTDMAH. From this study, The HEA is expected to be advantageous precursor for low temperature thin film deposition technique.

AF-MoP-4 Al Precursor with Low Growth Rate for Conformal Al_2O_3 Thin Film*, **Kyuhyun Yeom**, H. Lee, K. Mun, D. Ryu, J. Seok,* Hansol chemical, Republic of Korea

Al2O3 thin film is variously used for an encapsulation layers of display, blocking layers of NAND, and capacitor dielectric of dynamic random access memory(DRAM).

Trimethylaluminium(TMA) that highly reactive is usually used to make Al_2O_3 thin film. Howerver, TMA has pyrophoric which leads to difficult handling and non-safety.

In addition, it has a high growth per cycle(GPC), which is not pappropriate to the micro process such as the $ZrO_2/Al_2O_3/ZrO_2$(ZAZ) process of DRAM dielectric need to precise controllable deposition.

We designed an Al precursor that has non-pyrophoric and a low GPC compared to TMA. Al_2O_3 was deposited on SiO_2, and ozone was used as a reactant gas.

The source and reactant gas showed self-saturation, respectively, and a wide and flat ALD range of 100-340°C was shown.

GPC had about 65-70% of TMA. In addition, Al_2O_3 thin film properties we examined such as XPS, XRR, and TEM.

AF-MoP-5 Low-Temperature HfO_2 Gate Dielectric for Topological Insulator Devices*, P. Shekhar, S. Shamim, V. Hock,* Physikalisches Institut (EP3) and Institute for Topological Insulators, Universität Würzburg, Germany*; H. Buhmann, **Johannes Kleinlein**,* Physikalisches Institut and Institute for Topological Insulators, Universität Würzburg, Germany*; L. Molenkamp,* Physikalisches Institut (EP3) and Institute for Topological Insulators, Universität Würzburg, Germany

On this poster, we present details of our low-temperature (30 **°**C) hafnium oxide atomic layer deposition (ALD) process **[1].** We apply the layers as gate dielectrics in devices of the thermally sensitive topological insulator HgTe **[2,3]**. The gate structures are used to tune the charge carrier density in the HgTe quantum well. For the hafnium oxide deposition, we utilize a home-made reactor and TDMAH and water as precursor and reactant, respectively. Due to the low deposition temperature, the films can be patterned by lift-off processes. Here, we present the layout of our home-made reactor and a schematic of the complete ALD system. Furthermore, we show results of our investigations on the homogeneity of the hafnium oxide layer thickness over the whole sample stage area, as well as on long-term reproducibility. We provide details of our gate fabrication process, following a self-aligned lift-off process: Both the dielectric and the electrode are deposited successively using a single resist mask. We use standard photoresist technology for device dimensions in the micrometer range, and PMMA and electron beam lithography for nanostructure devices. Finally, we exemplary show applications of low-temperature hafnium oxide gate insulators in micro- and nanostructure devices, such as quantum spin hall effect devices **[4]**, HgTe-based superconducting devices **[5]**, and quantum point contact devices **[6]**. We analyze the gate performance in these devices, as well as leakage currents and gate hysteresis.

[1] Shekhar et. al, *ACS Appl. Mater. Inter.* **14**, 33960 (2022)

[2] Koenig et. al, *Science* **318**, 766 (2007)

[3] Roth et. al, *Science* **325**, 294 (2009)

[4] Bendias et. al, *Nano Lett.* **18**, 4831 (2018)

[5] Bocquillon et. al, *Nat. Nanotechnol* **12**, 137 (2017)

[6] Strunz et. al, *Nat. Phys.* **16**, 83 (2019)

AF-MoP-6 Silicon Nitride ALD Process Using High Purity Hydrazine for Low Temperature Deposition*, **Hayato Murata**, Y. Koda, Y. Wada, T. Kameoka,* Taiyo Nippon Sanso Corporation, Japan*; J. Spiegelman,* RASIRC*; N. Tomita,* Taiyo Nippon Sanso Corporation, Japan

High quality ALD silicon nitride (SiN) at low temperature is required for advanced device structure complexity. High purity hydrazine (N_2H_4) is a promising nitrogen source for low temperature ALD nitride process due to its high reactivity. We have reported various advantages of N_2H_4 for titanium nitride (TiN) film ALD process over the conventional ammonia (NH_3) process [1-2]. In this study, we found that N_2H_4, comparing to NH_3, was capable to have high quality SiN film at 550°C by ALD processing with dichlorosilane (DCS, SiH_2Cl_2). This result shows N_2H_4 instead of NH_3 has potential to be new nitrogen source for state-of-the-art devices.

In such low temperature region, purity of source is very sensitive for film quality. We used N_2H_4 of BRUTE Hydrazine (RASIRC, Inc.) which enabled safe delivery of high-purity N_2H_4 gas. SiN ALD process was experimentally evaluated by delivering DCS/N_2H_4 or DCS/NH_3 to a hot-wall tubular reactor. ALD SiN films using DCS/N_2H_4 were formed at 550-650°C.

GPCs (growth per cycle) in DCS/N_2H_4 ALD were found to be 0.49-1.27 Å/cycle while those in DCS/NH_3 ALD were 0.10-1.02 Å/cycle at 550-650°C. These results indicate that N_2H_4 could be available to further enhancement in throughput. In addition, refractive index (R.I.) of DCS/N_2H_4 film was about 1.90 at 550°C while R.I. of typical SiN was about 1.9-2.1. In contrast, R.I. of DCS/NH_3 film formed at 550°C was under 1.50 likely due to the formation of silicon oxide whose R.I. is around 1.45. Moreover, WER in dilute hydrofluoric acid (100:1 HF) of DCS/N_2H_4 film was 14.1 Å/cycle at 550°C. On the other hand, WER of DCS/NH_3 film formed at 550°C was twenty times higher (303.7 Å/cycle) compared with that of DCS/N_2H_4. These results indicate that N_2H_4 as higher reactive nitrogen source has an effect on SiN film quality at lower temperature.

In order to investigate reactivity of N_2H_4, activation energies (Ea) for nitriding reaction to the DCS chemisorption surface structure were calculated. The quantum chemical calculation was performed by B3LYP density functional with cc-pVDZ basis set. The Ea of N_2H_4 reaction with the DCS chemisorption structure was 31 kJ/mol while that of NH_3 reaction was 60 kJ/mol. These results indicate N_2H_4 is a higher reactive nitrogen source for surface than NH_3.

Thus, we concluded that N_2H_4 is very promising nitrogen source for ALD with high reactivity at low temperature and that N_2H_4 is practical option for ALD process development to be satisfied with both throughput and SiN film quality.

[1] D. Alvarez et al., PRiME2020, G02-1668 (2020).

[2] H. Murata et al., ALD/ALE2021, AF301 (2021).

AF-MoP-7 ALD Precursor Design for Post-Transition Metal Films*, **Atsushi Sakurai**, N. Yamada, T. Yoshino, A. Nishida, M. Hatase, M. Enzu, A. Yamashita, Y. Ooe, C. Mitsui,* ADEKA CORPORATION, Japan

This presentation will share the basic chemistry of potential ALD precursors in relation to the post-transition metals such as Zn, Ga, In, Sn, Pb, Sb and Bi. Most of those metals take p-block configurations and prefer low oxidation state from 2+ to 4+. Consequently, their ALD precursor and process design should be different from the early and late transition metals which have been very well investigated. For example, many organometallic compounds (with metal-carbon bonds) with post-transition metals could be isolated, stable and volatile even with simple and small ligand design, whereas early

and late transition metal (d-block) ones do not have enough thermal stability for ALD use. Also, we need to recognize that some of those compounds are pyrophoric (e.g. trimethylgallium, diethylzinc) and environmentally restricted due to adverse influence on human body (e.g. tetraethyllead). However, we can also say that metal amides (metal-nitrogen bond) with post-transition metals are not always stable. Zn bis(dialkylamide), In tris(dialkylamide), Pb bis(trimethylsilylamide) and Bi tris(dialkylamide) are thermally very unstable, whereas Ga tris(dimethylamide), Sn tetrakis(dialkylamide) and Sb tris(dialkylamide) are reasonably stable so as to be considered as ALD precursor candidates.

We will summarize the basic precursor data (TGA, DSC, etc.) of post-transition metal ALD precursors and will discuss the chemistry driving ligand selection leading to attractive vapor pressure, thermal stability and ALD reactivity.

AF-MoP-8 Correlating In-Situ Photoluminescence and Ellipsometry: A Novel approach to Analyze and Optimize ALD Materials for Photovoltaic Applications*, N. HARADA, A. LEVTCHENKO,* IPVF, France*; D. COUTANCIER,* CNRS, France*; F. DONSANTI,* IPVF, France*; J. GUILLEMOLES,* CNRS, France*; D. SUCHET,* Ecole Polytechnique - CNRS, France*; G. DELPORT,* ***Nathanaelle SCHNEIDER****,* CNRS, France

For the last decades, Atomic Layer Deposition (ALD) has undoubtedly become a key technique to deposit thin films in various research fields. As the deposition is sequential and self-limited, a high control over the films' thickness can be reached together with a high conformality. Moreover, the deposition can be done at low temperatures (below 100 °C) and allows the growth of a large panel of materials on different substrates. In the field of PV, ALD films are already used at an industrial scale (for instance in PERC solar cells) but their use also extends to buffer layers for CIGS cells, transparent conductive oxides (TCO), passivation or charge transport layers (ETL & HTL) for perovskite solar cells … [1]

In-situ ellipsometry together with photoluminescence (PL) were considered as relevant techniques to correlate film's growth properties and its functionalization. Indeed, by acquiring Spectroscopic Ellipsometry (SE) data, the film's thickness and optical constants are addressed during the growth [2], while its function is determined by analysing PL spectra or PL decays (by Time Resolved Photoluminescence TRPL) [3]. While in-situ SE is commonly used during ALD growth, only one example of in-situ PL has been developed to our knowledge and none combines the two techniques [4], making our approach original. In-situ characterizations would also be very useful for pre-industrialization, by reducing the number of samples required to totally take advantages of ALD specificities and generate highly performant devices. This presentation will introduce our experimental set-up in more details, as well as some first analysis results on the growth of ALD thin films on solar cells correlating SE and PL measurements (Fig. 1).

1. "Atomic Layer Deposition (ALD). Principes Généraux, matériaux et applications" *Ouvrage spécial desTechniques de l'Ingénieur : Principes et applications de la technique ALD (Atomic Layer Deposition)*
2. Langereis, E. *et al.J. Phys. Appl. Phys.***42**, 073001 (2009).
3. Unold, T. & Gütay, L. in *Advanced Characterization Techniques for Thin Film Solar Cells* -275–297.
4. Kuhs, J. *et al.ACS Appl. Mater. Interfaces***11**, 26277–26287 (2019).

AF-MoP-9 Chemistry of Boronic Acids on Semiconductor Surfaces: Pathways to Organic Monolayer Resists and Single Molecule Inhibitors for AS-ALD*,* ***Dhamelyz Silva Quinones****, A. Teplyakov,* University of Delaware

As the size of the components in electronic devices is shrinking, new approaches and chemical modification schemes are needed to produce nanometer-size features with bottom-up manufacturing.

Organic monolayers can be used as effective resists to block the growth of materials on non-growth substrates in area-selective deposition methods, particularly in AS-ALD. At the same time, same or similar organic molecules can act as small molecule inhibitors (SMIs) introduced during the ALD process.

This study aims at investigating the chemistry of boronic acids that can be used to make such resists on oxide and elemental semiconductors. We use 4-fluorophenylboronic acid (FPBA) as a model to investigate the reaction of boronic functionality with surfaces of TiO_2 and Al_2O_3 nanomaterials and with a functionalized Si(100) surface. On oxides surfaces, the reaction involves a condensation between a boronic acid functionality and the surface hydroxyl groups. On a Si(100) surface, the reaction is determined by surface termination. We use Cl-terminated Si(100) surface as an example to follow the reaction. The coverage of boronic acid attached to all these materials is the key to evaluate its potential as a blocking resist for ALD. Microscopy (AFM) and spectroscopy (ToF-SIMS, XPS, IR, and solid-state NMR) methods, together with cluster model DFT calculations are used to understand the chemical nature and surface bonding of FPBA on all these model surfaces. A commercial thermal ALD of TiO_2 based on TDMAT and water is used to test the reactivity of functionalized silicon surfaces and the potential of FPBA to be used as a non-growth resist. A possibility to use boronic acids as SMIs is also discussed.

AF-MoP-10 Trench Coverage Properties of Oxide Films Deposited at Low Temperature by Pure Ozone ALD*, N. Kameda, T. Hagiwara,* ***Soichiro Motoda****,* MEIDEN NANOPROCESS INNOVATIONS, INC., Japan*; K. Nakamura, H. Nonaka,* AIST, Japan

We report improvement of trench coverage of Al_2O_3 and SiO_2 films deposited by ALD using a pure ozone gas (PO-ALD) at low temperatures.

Pure ozone gas has a higher concentration of O_3 gas(≥99 vol%) than in the conventional ozone gas (<10 vol%).In this gas, high purity is achieved, while NO_x and heavy metal contaminants are 3-4 orders of magnitude lower compared to the conventional ozone gas. Thus, it is an effective oxidation source for producing high-quality oxide films at low temperatures. For example, Al_2O_3 film using PO-ALD with TMA precursor has low carbon content below detection limit by XPS at 150°C [1].

Another feature of an ozone molecule in the gas phase at the pressure range (up to 1000 Pa) during the PO-ALD process is its long half-life time, which is calculated from rate constant of its chemical reaction to be over 1000 seconds at 150°C. This half-life time is far longer than exposure time to the oxidant gas within each ALD cycle (< 100 seconds). Therefore, improvement in productivity during batch processing and improvement in trench coverage can be expected by supplying ozone without any decomposition to the inner part of trenches with high aspect ratios.

To confirm this expectation, Al_2O_3 film was deposited by PO-ALD with TMA for the trench with an aspect ratio of 55 (width 2.4um and depth 134um). The coverage, defined as the ratio of oxide thickness at the trench bottom to that at the trench top, was 0.52 and 0.98 at deposition temperatures of 100 and 300°C, respectively. At an ALD window temperature of 300°C, where TMA can be uniformly adsorbed to the bottom of the trench, PO-ALD can be formed on the bottom of the trench as well as on the top. On the other hand, at 100°C, which is lower than the ALD window, the amount of TMA adsorption was different between the top and the bottom of the trench, leading to the decrease in the coverage. However, if we compare each of GPC at the bottom of trench (GPC_{bottom}), the GPC_{bottom} of PO-ALD at 100°C was 0.076 nm/cycle, which is still larger than that of ALD using H_2O and O_2 plasma (0.064 and 0.056 nm/cycle) under the same condition for supplying the precursor gas. These results indicate that PO-ALD is so effective as to more homogeneous oxidation inside the trench structure with its higher reactivity even at the trench bottom compared to other oxidant gases.

We will also report and discuss trench coverage with a higher aspect ratio such as that over 100 and the case with SiO_2 films.

[1] N. Kameda, T. Hagiwara, A. Abe, T, Miura, Y. Morikawa, M. Kekura, K. Nakamura, and H. Nonaka, ALD/ALE 2020 Virtual meeting, Poster presented at AF+MoP69 (2020).

AF-MoP-11 Novel Volatile and Liquid Sc Precursors for Electronic Applications*, M. Kapitein, S. Herritsch, M. Balmer, T. Hepp, E. Schlathoelter,* ***Oliver Briel****, J. Koch,* Dockweiler Chemicals, Germany

Scandium (Sc) based materials are gaining increased attention in research labs evaluating devices for electronic applications. The continuous down-scaling of transistors demands new materials that meet the stringent requirements of semiconductor devices. Sc-based oxides are discussed to replace HfO2 as dielectric in metal gate and additionally, these oxides show good etch properties[1]. A new field of research is (Al,Sc)N MOCVD, which could disrupt power and rf signal processing device performance if successful[2]. However, conventional Cp3Sc is a solid-state precursor with relatively low vapor pressure, hampering the application of Sc-based materials. Other alternatives show complicated synthesis routes or may contain species that are unfavorable for a certain process.

Here we present a series of newly developed Sc-based precursors for CVD and ALD applications. Compared to commonly known Cp3Sc, the Sc precursors are liquid showing an increased vapor pressure, therefore improving vapor formation under process conditions. Molecule structures and thermogravimetric data are discussed.

[1]de Rouffignac, P., Yousef, A. P., Kim, K. H. & Gordon, R. G. ALD of Scandium Oxide from Scandium Tris(N,N[sup ']-diisopropylacetamidinate) and Water. Electrochemical and Solid-State Letters 9, F45 (2006) doi: 10.1149/1.2191131.

[2]Streicher, I. et al. Enhanced AlScN/GaN Heterostructures Grown with a Novel Precursor by Metal–Organic Chemical Vapor Deposition. physica status solidi (RRL) – Rapid Research Letters 2200387 (2022) doi: 10.1002/pssr.202200387.

AF-MoP-12 PEALD Growth of Doped Indium Oxide Films with Control Over the Film Composition and Properties by Supercycle Approach Implementation*, M. Zered,* ***Valentina Korchnoy****, K. Weinfeld, G. Frey, M. Eizenberg,* Technion - Israel Institute of Technology, Israel

This investigation explored composition and physical properties of doped In_2O_3 films deposited on glass or thermal oxide substrates at temperature 220°C in an Ultratech Fiji G2 PEALD System. Sn, Ti and Mo were examined as potential dopants for In_2O_3.Doping was performed using supercycle of In precursor and dopant precursor. In precursor was delivered in multipulse mode by a sequence of two consecutive pulses in a quick succession, to extend precursor residence time. Doping level was controlled by varying dopant cycles to In cycles ratio. A schematic diagram of the process is shown in Fig1. Growth per cycle rates for doped materials (ITO, ITiO and IMoO) and pure materials depending on the cycle ratio are presented in Tables1,2. Doped materials growth rates are in good agreement with ones calculated using Rule of Mixtures. Fig2,3 show Sn/In and Ti/In atomic ratio extracted from XPS depth profile for 1:12 and 1:20 films deposited on SiO_2. For ITO, the deposited atomic ratio is very close to Sn:In cycle ratio used in the process and is in good agreement with Rule of Mixtures. For ITiO, extracted from XPS Ti atomic ratio is higher than its ratio in the supercycle recipe and deviates from Rule of Mixtures.

Electrical measurements Fig4, show that introducing dopants to In_2O_3 films causes resistivity changes: for ITO resistivity drops by~ an order of magnitude. For ITiO resistivity rises for heavily doped films and decreases along with decrease of Ti cycle ratio. Optimal conductivity was reported for 2-3% of Ti

Thermal annealing of deposited films was carried out in N_2 atmosphere, at temperature 400°C, for 10 minutes. Thermal treatment has greatly lowered resistivity by 1-3 orders of magnitude for all films, Fig4. Lowest resistivity achieved for Sn-doped, Ti-doped, and Mo-doped were $2.8{\cdot}10^{-4}\Omega$cm, $4.2{\cdot}10^{-4}\Omega$cm and $6.1{\cdot}10^{-4}\Omega$cm respectively. The drop in the film resistivity for undoped In_2O_3 film can be explained by generation of O vacancies, which effectively increase carrier concentration. Optical changes were measured by transmission spectrophotometry, Fig5. Transmission decrease in IR region after annealing is attributed to free charge carrier absorption in conduction band due to dopant activation. Absorption edge shift towards lower wavelengths (Moss-Burstein effect), related to the filling of conduction band states, is observed for the annealed films. Mo-doped and Ti-doped films exhibit superior IR transparency over the conventional Sn-doped films

Supercycle approach based on indium and dopant cycle ratios was successfully employed to produce doped In_2O_3 films with control over the films composition and properties

AF-MoP-13 Using Glow-Discharge Optical Emission Spectroscopy to Characterize Polymers Treated Through Vapor Phase Infiltration*,* ***Seancarlos Gonzalez****, Y. Choe, D. Bergsman,* University of Washington

Vapor phase infiltration (VPI) is a variation of atomic layer deposition (ALD) which takes advantage of long hold times to allow reactants to diffuse into a porous substrate. Recently, VPI has been used for the post-synthesis modification of polymers by infusing metal oxides into the polymer matrix to improve crucial membrane properties such as solvent stability and separation performance. However, characterizing polymers modified by infiltration, such as the depth and concentration of infiltrated reactants, can be challenging. Ellipsometry can be used to characterize surface thickness, but it cannot determine the depth to which the infiltration is successful or the elemental composition as a function of thickness. Cross-sectional scanning electron microscopy (SEM) can determine elemental composition, but its resolution for certain elements is limited to only very thick layers. X-ray photoelectron spectroscopy (XPS) can depth profile to determine elemental composition, but this technique is extraordinarily time and cost intensive.

In this work, we examine the use of glow-discharge optical emission spectroscopy (GD-OES) to characterize polymer membranes treated by infiltration. This technique uses plasma to sputter a crater into a sample, and then measure the atomic emissions of the sputtered elements. Signals are produced for each element as a function of time, which can yield quantitative data of elemental composition as a function of depth when calibrated to a standard. We demonstrate the use of GD-OES to explore the effectiveness of VPI on thin polymers by determining the depth to which infiltration was successful and comparing the elemental compositions of polymers infiltrated under different conditions.

AF-MoP-14 New Approaches for the Thermal Atomic Layer Deposition of Elemental Antimony Thin Films*,* ***Daniel Beh****,* Wayne State University*; Z. Devereaux, T. Knisley,* Applied Materials*; C. Winter,* Wayne State University

Elemental antimony (Sb) thin films have applications in phase change memory, doping of semiconductors, and as precursors to Sb-containing materials. Atomic layer deposition is an important thin film growth technique that can afford Angstrom-level thickness control and perfect conformality in high aspect ratio features. Many applications of Sb films require growth in substrates with nanoscale features where perfect thickness uniformity and conformal coverage are required. Accordingly, the growth of Sb films by ALD is an important research goal. Elemental Sb films have been previously grown by thermal ALD using $SbCl_3$ and $Sb(SiEt_3)_3$[1] and $Sb(SiMe_3)_3$ and $SbCl_3$.[2] We have previously reported the use of 2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene (**1**) or 1,4-bis(trimethylsily)-1,4-dihydropyrazine (**2**) as reducing co-reactants in ALD.[3] Herein, we describe the thermal ALD of elemental Sb films using $SbCl_3$ and **1** or **2** as the co-reactants. Most deposition experiments were conducted using **2** as the co-reactant, since it is more reactive than **1**. Sb films were deposited at substrate temperatures between 75 and 150 ºC using $SbCl_3$ and **2** as precursors. At a substrate temperature of 75 ºC, a growth rate of 0.58 Å/cycle was observed on Si-H substrates. The X-ray diffraction pattern of a 28 nm thick film on an Si-H substrate matched the reference pattern for elemental Sb. X-ray photoelectron spectroscopy of a 28 nm thick film on Si-H afforded a composition of 98.5% elemental Sb after 20 minutes of argon ion sputtering. Other properties of the Sb films will also be described. Finally, we will present alternative halogen-free Sb precursors and nitrogen-based co-reactants that also afford elemental Sb films in thermal ALD processes.

1. Pore, V.; Knapas, K.; Hatanpää, T.; Sarnet, T.; Kemell, M.; Ritala, M.; Leskelä, M.; Mizohata, K. Chem. Mater. 2011, 23, 247−254.

2. Al Hareri, M.; Emslie, D. J. H. Chem. Mater. 2022, 34, 5, 2400–2409.

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

AF-MoP-15 Electron Beam Generation and Precise Control of Beam Energy for Large Area Electron Enhanced Atomic Layer Deposition*,* ***MINSEOK KIM****, J. Jung, J. Park, C. Lim, B. Seo, C. Chung,* Hanyang University, Republic of Korea

A large-area electron beam is generated, and the electron beam energy is precisely controlled using several DC grids. As the electron beam source's electron temperature is lowered (T_e =2.43 eV to 0.8 eV), the electron beam's energy spread is reduced from 7.8 V to 2.7 V. This is because the low electron temperature plasma has a narrow electron energy distribution, which makes the energy spread of the generated electron beam smaller. Through precise control of the electron beam energy, the generation of N and F radicals according to the beam energy is observed in Ar/N2 and Ar/CF4 plasmas. It is expected that a precursor decomposition and ligand formation can be selectively made in the electron-enhanced ALD process through precise control of the large-area electron beam.

AF-MoP-16 Development of Piezo Controlled Vapour Delivery System for Ru ALD Application*,* ***Hiroshi Nishizato****,* HORIBA STEC, Co., Ltd., Japan*; G. Krunal,* HORIBA STEC, Co., Ltd., India*; T. Moriyama,* HORIBA STEC, Co., Ltd., Japan*; K. Uesugi,* Hiroshima University, Japan*; G. Rahman,* Hiroshima University, Bangladesh*; P. Lowery, T. Freeman,* HORIBA Reno Technology Center*; Y. Amemiya, A. Teramoto,* Hiroshima University, Japan

Atomic layer processes, such as atomic layer deposition (ALD) use precursors. Some of the Metal ALD process uses rare metal such as Ru for metal connection.This kind of metal organic chemical vapor used in ALD

processes has to be delivered at a constant volume, and concentration per pulse, without wasting unused precursor through the vent lines during purge cycles. In the present study, the newly developed fast response flow-controlled vapor delivery system using a piezoelectric actuated electromechanical valve (EMV) was developed and implemented for this ALD application. This valve shows a response time of <1ms for ON/OFF pulsing and <10ms for the flow control with the ability of programable waveform control. Ruthenium film formation has been confirmed from Ru precursor and Oxygen on the oxidised Si surface by using this piezo actuated electromechanical valve (EMV).Fig. 1 shows a Tool configuration and setting of Ru ALD. In the configuration shown, no ruthenium precursor vent lines are used and ruthenium precursor dosing goes directly to the reactor in the ALD cycle.

AF-MoP-17 Realization of Conductive Electrodes for Solar Cells by Spatial ALD Using New Coinage Metal Precursors*, N. Boysen,* Ruhr University Bochum, Germany*; T. Hasselmann, B. Misimi,* University of Wuppertal, Germany*; M. Karppinen,* Aalto University, Finland*; T. Riedl,* University of Wuppertal, Germany*; **Anjana Devi,*** Ruhr University Bochum, Germany

The realization of conducting and transparent ultra-thin metallic films by ALD remains a major challenge due to a pronounced Volmer-Weber type island growth on different substrates. Several applications that are relying on thin metallic films, such as transparent electrodes for solar cells, might not be easily accessible by ALD, as precursors with suitable characteristics are missing. Especially for the deposition of metallic silver films by ALD, a precursor possessing high thermal stability, volatility and reactivity is still sought after. Based on our iterative efforts in terms of ligand engineering, new copper and silver precursors were developed and their successful application in low-temperature plasma-assisted spatial ALD processes at atmospheric pressure (APP-ALD) was demonstrated.[1] Introducing the stabilizing N-heterocyclic carbene ligand (NHC), combined with reactive anionic counterparts such as hexamethyldisilazides (hmds) or β-diketonates (acac), copper and silver precursors and their respective processes for metallic thin films could be established.[2] The new silver precursor [Ag(NHC)(hmds)] provides a significantly enhanced reactivity compared to its commercially available counterpart [Ag(fod)(PEt_3)] (fod: 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate), which enables spatial ALD processes with H_2/Ar plasma at a record-low deposition temperature of 60 °C. This not only significantly reduces the total thickness of the layers needed for percolated and thus conductive silver films, but also enables an application of the silver films as conductive electrodes in organic solar cells.[3] Furthermore, new ALD processes based on the NHC-stabilized copper precursors, namely [Cu(NHC)(hmds)] and [Cu(NHC)(acac)] were established. Using [Cu(NHC)(hmds)] and H_2/Ar plasma, pure and conductive copper films were deposited at a low deposition temperature of 100 °C by APP-ALD.[4] Also, in a thermally-driven ALD process with [Cu(NHC)(acac)] and hydroquinone, nanoparticulate metallic copper deposits could be obtained at remarkably low deposition temperatures of 145 °C to 160 °C. These new findings reiterates that deposition of conductive copper or silver thin films at low temperatures can only be realized by a rational design of highly reactive precursors that are tailor-made for such demanding processes.[5] This contribution summarizes the main findings of precursor and process development at RUB, BUW and Aalto University over the last years and presents ideas on how to further strengthen the precursor and process characteristics for different applications.

AF-MoP-19 Comparative Study of the Surface Reactivity and PEALD of Monoaminosilanes and Cyclic Azasilanes*, **Chad Brick**, T. Ogata, J. Collins,* Gelest, Inc

In this work, we report the physical properties, surface reactivity and plasma-enhanced atomic layer deposition (PEALD) of a series of monoaminosilanes and cyclic azasilanes, with a focus on the relationship between chemical structure and properties such as vapor pressure, pulse times required to reach surface saturation, practical material consumption rates in a production-like tool, and water contact angle. Additionally, the conversion of these chemical structures to SiO_2 using oxygen plasma PEALD will be discussed in terms of growth per cycle, the required temperature and plasma pulse times for conversion to oxide, and the resulting film composition and properties.

AF-MoP-20 Atomic Layer Deposition of Strontium Oxide on Different Materials*, **Marek Eliáš**,* CEITEC, Brno University of Technology, Czechia*; A. Harumningtyas,* Osaka University, Japan*; D. Nečas, L. Janů, E. Dvořáková,* CEITEC, Czechia*; T. Ito, P. Vinchon, S. Hamaguchi,* Osaka University, Japan*; L. Zajíčková,* CEITEC BUT & Masaryk University, Czechia

Atomic layer deposition (ALD) on different substrates is challenging because of its extreme surface-chemistry sensitivity given by the targeted ALD self-limiting nature. In this study, we investigated the growth of strontium oxide from bis(tri-isopropylcyclopentadienyl) strontium $Sr(iPr_3Cp)_2$(98%, Strem, Massachusetts, USA) using either H_2O oxidation step in thermal ALD or oxygen plasma step in plasma-enhanced ALD. The primary motivation was to prepare strontium-containing films for spinal implants. Strontium has a dual effect of stimulating osteoblast function and inhibiting osteoclast function and can be used for osteoporosis treatment. In combination with TiO_2, a typical biocompatible material, it can enhance the bioactivity of coated implants. The combination of SrO with TiO_2 is also advantageous in other applications. The ternary strontium titanate $SrTiO_3$ is of significant interest for high-density metal−insulator−metal (MIM) capacitors. $SrTiO_3$ perovskite applications span from electronics to energy. Thus, it is essential to understand how ALD of SrO works on different materials either because of the need to fine-tune the composition of ternary oxides or create thin-film heterostructures. Polymer substrate brings an additional challenge to the ALD processes. We studied the ALD of SrO on Si, Ti, TiO_2, and polyetheretherketone (PEEK) with different surface treatments. The selection of the PEEK substrate was motivated by applications for spinal implants because its elastic modulus is similar to the human cortical bone.

AF-MoP-22 Effects of Silicon Surface Termination on the Initial Stages of TiO_2 Deposition by ALD*, **Tyler Parke**, A. Teplyakov,* University of Delaware

As atomic layer deposition (ALD) emerges as a method to fabricate architectures with atomic precision, emphasis is placed on understanding surface reactions and nucleation mechanisms. ALD of titanium dioxide with $TiCl_4$ and water has been used to investigate deposition processes in general, but the effect of surface termination on the initial TiO_2 nucleation lacks needed mechanistic insights. Further, a wider toolkit of terminations, which promote or inhibit nucleation, may allow for more elaborate deposition schemes involving the same overall deposition chemistry. This work examines the adsorption of $TiCl_4$ on Cl-, H-, and -OH terminated silicon single crystal surfaces to elucidate the general role of different surface structures and defect types in manipulating surface reactivity of growth and non-growth substrates. Other surface terminations derived from these starting points, specifically additional modification step with primary amines, were also tested. The surface sites and their role in the initial stages of deposition are examined by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Density functional theory (DFT) computations of the local functionalized silicon surfaces suggest oxygen-containing defects are primary drivers of selectivity loss on most of these surfaces.

AF-MoP-24 Deposition Characteristics Evaluation of New In Precursor for IGZO TFT*, **Yong Hee Kwone**, S. Jeon, S. Lee, T. Byun, Y. Im, S. Lee,* DNF Co. LTD., Republic of Korea

In accordance with the high resolution/high integration of the display market, the required performance of the driving element required for the back-plane is increasing in order to secure uniform performance in a large area.

Accordingly, various studies on materials and processing methods of TFT devices are being conducted. In particular, as a material for TFT, IGZO based on In_2O_3, which has the advantages of relatively high mobility compared to amorphous silicon, excellent uniformity compared to polycrystalline silicon, and a simple manufacturing process, has been actively studied. However, conventional indium precursors have disadvantages of high price as well as low vapor pressure and low deposition rate.

In this study, the deposition characteristics of In_2O_3 were evaluated using the newly developed Indium precursor (DIP-4) for the purpose of dramatically improving the disadvantages of the existing Indium precursor (Fig 1). In addition, it was compared with DADI((3-Dimethylaminopropyl)dimethylindium), a currently commercialized indium precursor.

The deposition process used the PEALD process, which is easy to control the composition and excellent in thickness uniformity in the deposition of a multi-component thin film with a multi-layer structure. As a result of evaluating the basic ALD characteristics (Saturation, Window, etc.) of the DIP-4 and DADI, In_2O_3 deposited with each Precursor showed similar characteristics (Composition, Density, Crystal Structure). However, the

deposition rate of the DIP-4 was about 35% higher than that of DADI(Fig 2).Through this, the high productivity of the DIP-4 was confirmed.

In addition, the DIP-4 is advantageous in terms of unit price because it can be obtained with simplified synthesis and high yield by distillation.

For the formation of multi-layered IGZO thin films, the incubation time, deposition rate, and interface characteristics of In_2O_3 deposited with the DIP-4 were evaluated according to the surface (Ga_2O_3, ZnO).

AF-MoP-27 Atomistic Study of Amorphous Si-O-X Networks for Plasma Enhanced Atomic Layer Deposition-Produced SiO_2 Films: Illuminating the Structure-Composition-Mechanical and Electrical Property Connections*, A. Dernov,* University of Minnesota, USA*; P. Agarwal, R. Kumar,* Lam Research Corporation*; **Traian Dumitrica**,* University of Minnesota, USA

Using self-consistent density functional tight-binding simulations it is shown that Aluminum (Al) content in amorphous silica (*a*-SiO2) changes its ideal microscopic structure in a manner compatible with densification. Similar to the structure of pressure-densified *a*-SiO2, the Al-modified *a*-SiO2 comprises a network of Silicon (Si)-centered tetrahedra as well as unquenchable pentahedra and, to a smaller extent, hexahedra coordination defects. Al itself acts not only as a network former, with fourfold coordination but also as a center for fivefold and sixfold coordination defects. Al content promotes densification since it shifts the potential energy minima at densities larger than in their pristine counterpart. Calculations uncover that Young's modulus (Y) and static dielectric constants ($\varepsilon 0$) can be effectively doubled through densification. Oxygen starvation promotes network polymerization, which further increases Y and $\varepsilon 0$. However, the small ring formation through Si–Si bonding and the presence of undercoordinated Si introduce electronic states in the electronic band gap. The results provide guidance for the bottom-up design of amorphous silica with tunable microscopic structure and properties desirable for advancing electronic applications.

AF-MoP-28 Surface Modification of 2,6 Diamino-Pyrazine-1-Oxide by Atomic Layer Deposition of Al_2O_3*, **John Miller**, R. Reeves,* Lawrence Livermore National Laboratory

Inkjet additive manufacturing utilizes a stream of solid particles embedded in a cross-linking fluid which is ejected from a nozzle and stacked layer by layer to make custom shapes with tunable properties. The properties of the printed components are highly dependent on the solid content capable of being loaded into the inks. Atomic layer deposition (ALD) provides a means to modify the surface of particles to reduce their surface energy and thus cohesivity in inkjet solutions, allowing for increased solids loading. This work investigates the effects of ALD Al_2O_3- on the surface of dry 2,6 Diamino-Pyrazine-1-Oxide (DAPO) particles, which can be used as a solid filler in ink solutions. In bulk quantities, powder rheometry was utilized to measure the basic flowability energy of coated DAPO as a function of ALD cycles. Results show that increasing the number of coating cycles increases the basic flowability energy, indicating a decrease in overall powder cohesivity. Small samples of uncoated and coated DAPO were also measured by Inverse Gas Chromatography to directly measure changes in surface energy before and after coating. Results showed that surface coatings reduce the surface energy at low gas coverage corresponding to saturation of high energy sites on the surface of the DAPO.

AF-MoP-29 Precise Interface Engineering for High Thermoelectric Performance in CuNi Alloys Using Powder ALD*, S. He,* Leibniz Institute for Solid State and Materials Research, Germany*; A. Bahrami,* Helmholtzstraße 20, Germany*; S. Lehmann, **Kornelius Nielsch**,* Leibniz Institute for Solid State and Materials Research, Germany

In thermoelectric materials, interfaces of phase boundaries play a critical role in carrier/phonon transport. Herein, we present a strategy for designing a sandwich coating structure based on powder atomic layer deposition (pALD) to precisely control and modify the phase boundaries of CuNi alloys, and thus decouple thermoelectric parameters. Ultrathin interlayers of ZnO and Al2O3 oxides are uniformly deposited on the phase boundary of CuNi alloys to demonstrate the effectiveness of this strategy. The hierarchical deposition of ZnO and Al2O3 layers contribute to the creation of an energy barrier, that augments the Seebeck coefficient significantly. Despite a slight decrease in the electrical conductivity, the enhanced Seebeck coefficients for 50 cycles ZnO coated samples compensated for the loss, resulting in a ~45% increase in power factor over the uncoated sample. Thereupon, the sandwich-like multiple layers structure (ZnO/Al_2O_3/ZnO) was built to enhance electrical resistance at phase boundaries. Beyond 50 ALD cycles, the multiple-layered structure sustained the increased power factor while notably reducing thermal conductivity. In the sample with 44 cycles ZnO/11 cycles Al_2O_3/ 44 cycles ZnO cycles multi-layer structure, a maximum figure of merit (zT) of 0.22 was achieved at 673 K. Due to the decoupling of thermoelectric parameters by ALD, the zT value increased 144% when compared to pristine CuNi and is nearly as high as previously reported values. The ALD-based approach to decoupling thermoelectric parameters is easily applicable to other thermoelectric materials, resulting in the development of high-performance materials.

AF-MoP-30 High-Throughput SiO_2 PEALD Using a Novel Si Precursor*, **Jin Sik Kim**, B. Kim, J. Choi, W. Koh,* UP Chemical Co., Ltd., Republic of Korea

A newly developed Si precursor can enhance SiO_2 PEALD throughput greatly. A notable application of SiO_2 PEALD is double patterning, for which SiO_2 film is deposited over photoresist at low temperature between room temperature and 150°C.The PEALD growth-per-cycle using the novel Si precursor is 2.3 times larger than bis(diethylamino)silane (BDEAS) and 1.7 times larger than diisopropylaminosilane (DIPAS) using O_2 plasma at 125°C. It may enhance productivity of PEALD double patterning process 2.3 or 1.7 times compared to using BDEAS or DIPAS. PEALD deposition characteristics and SiO_2 film properties including film step coverage, thickness uniformity, wet etch rate, carbon content, etc. deposited from the novel precursor and conventional ones such as BDEAS, DIPAS and BTBAS are presented and compared. The novel Si precursor shows the same or better characteristics.

AF-MoP-31 Oxidation Mechanism of Atomic Layer Deposition of HfO_2 Using O_3*, **Soo Hyun Lee**, B. Shong,* Hongik University, Republic of Korea

As the size of semiconductor device is shrinking down to the ultimate limit, there have been needs for deposition techniques that can control the thin films at atomic scale. Atomic layer deposition (ALD) is a powerful deposition technique that can fabricate thin film in excellent conformality even on substrates with high aspect ratio geometries. Hafnium oxide (HfO_2) is a representative thin film material that is often deposited via ALD due to its high k value and superior properties as dielectric. For ALD of HfO_2, commercialized Hf precursors containing amido ligands such as TEMAH (tetrakis(ethylmethylamino) Hf) and CpHf (tris(dimethylamido)cyclopentadienyl Hf) are often used. While TEMAH or other homoleptic amido precursors allow ALD using either water (H_2O) or ozone (O_3) as counter-reactants, the heteroleptic CpHf require oxidants stronger than H_2O such as O_3 in order to reduce carbon impurities [1,2]. Regardless of popular adaptation of O_3 as oxidant in oxide ALD processes, however, the chemical mechanism for the reaction of O_3 during HfO_2 ALD has not been elucidated yet. In this study, the oxidation mechanism of surface-adsorbed Hf precursors by O_3 is analyzed using density functional theory (DFT) calculations. Multiple possible oxidation reaction pathway which successfully removes remaining amido ligand on Hf are considered. Reaction of O_3 are expected to occur through multiple elementary steps, finally forming -OH moieties and remove C/H/N via liberation of several byproducts. Overall these reactions are found to be highly exothermic, possibly due to high reactivity of O_3.

References [1]JVSTA2012,30 (1),01A119. [2] JVSTA2017,35 (1),01B130.

AF-MoP-32 Eggshell-Type Catalysts by Atomic Layer Deposition: Distribution of Zinc Oxide Within Mesoporous Alumina Spheres*, **Jihong Yim**,* Aalto University, Finland*; N. Heikkinen,* VTT Technical Research Centre of Finland*; E. Haimi, C. Gonsalves, A. Chahal, J. Velasco, R. Karinen,* Aalto University, Finland*; J. Lehtonen,* VTT Technical Research Centre of Finland*; R. Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) is an intriguing method for preparing heterogeneous catalysts with well-defined surface structures.[1,2] A recent study by Arandia et al.,[3] related to this work, demonstrated the potential of zinc acetylacetonate [Zn(acac)$_2$] as an ALD reactant for tuning the surface properties of mesoporous zirconia-supported copper. In this work, we aim (i) to prepare a uniform coating of zinc oxide (ZnO) on mesoporous alumina (Al_2O_3) in a fixed bed flow type ALD reactor and (ii) to control the penetration depth of ZnO coatings on Al_2O_3 spheres by adjusting the dose of Zn(acac)$_2$.

ZnO was added on porous Al_2O_3 with an irregular shape (particle size ca. 0.1 mm) and Al_2O_3 spheres (particle sizes 1.0, 1.8 and 2.5 mm) in F-120 ALD reactor. The Zn(acac)$_2$ (vaporized at 120 ℃) was chemisorbed on calcined supports at 200 ℃ for 3 h in the ALD reactor. The leftover ligands after the chemisorption were oxidatively removed in synthetic air in a tube furnace at 600 ℃. Information on ZnO ALD on Al_2O_3 was obtained by inductively coupled plasma-optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS), and in-situ diffuse reflectance infrared Fourier transform spectroscopy-mass

spectrometry (DRIFTS-MS). By EDS analysis, a uniform zinc signal was observed throughout the 0.1 mm Al_2O_3 particle (Fig. 1 of supporting information). Zinc loading was ca. 3.1 wt% (1.8 Zn/nm^2). Meanwhile, zinc was observed near the outer surface of the Al_2O_3 spheres (Fig. 2). The penetration depth of the ZnO and the zinc loading increased (highest ca. 2.5 wt%) while increasing the dose of $Zn(acac)_2$ was directed through the support bed. These results indicate that the reaction of $Zn(acac)_2$ on Al_2O_3 spheres did not reach saturation yet. DRIFTS-MS showed that acac ligands adsorbed on Al_2O_3 were removed as CO_2 up to 550 ℃. The surface coverage profile of zinc coating on sphere support was simulated by a diffusion-reaction model fitted for various exposures, comparing well with experimental data (Fig. 3). We believe that the ALD process can be used to prepare eggshell-type heterogeneous catalysts.

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References

1. van Ommen, R.; Goulas, R.; Puurunen, R.L. *Atomic layer deposition, in Kirk-Othmer Encyclopedia of Chemical Technology* **2021**.

2. O'Neill, B. et al. *ACS Catal.* **2015**, *5*, 1804-1825.

3. Arandia, A. et al. *Appl. Catal. B* **2022**, *321*, 122046.

AF-MoP-33 Numerical Simulation of Surface Reactions During Plasma-Enhanced Atomic-Layer Deposition (PE-ALD) of Silicon Nitride (SiN), *J. Tercero,* Osaka University, Japan*; M. Krstić,* Karlsruhe Institute of Technology (KIT), Germany*; A. Jaber, E. Tinacba, N. Mauchamp, M. Isobe, T. Ito, K. Karahashi, **Satoshi Hamaguchi,*** Osaka University, Japan

Fabrication methods of high-performance semiconductor devices have reached a stage where precise processes with atomic-scale accuracy are required. As such, plasma-based surface processing techniques such as plasma-enhanced atomic layer deposition (PE-ALD) have been widely employed to deposit highly conformal thin films on surfaces with complex geometries. Each cycle of PEALD typically consists of self-limiting adsorption and desorption steps.[1] For example, in the case of silicon nitride (SiN) PE-ALE[2], chlorosilanes are adsorbed on the SiN surface at an elevated temperature. This study first analyzed the desorption process of chlorosilanes (SiH_xCl_{4-x}) on the Si(100):2´1 surface, using density-functional-theory (DFT) simulation, evaluating the adsorption and activation energies of chlorosilanes. It is observed that most chlorosilanes are dissociatively adsorbed on the surface barrierlessly even at zero surface temperature. We also performed classical molecular dynamics (MD) simulations to evaluate the adsorption reaction (sticking) probabilities of chlorosilanes on Si and SiN surfaces. Molecular dynamics simulation was also performed to study the nitridation step where the surface is exposed to nitrogen/hydrogen or ammonia plasmas. It was found that hydrogen radicals play an important role in removing excess chlorine (Cl) atoms from the surface.

References

[1] K. Arts, *et al.*, "Foundations of atomic-level plasma processing in nanoelectronics," Plasma Sources Sci. Technol. **31**, 103002 (2022).

[2] T. Ito, *et al.*, "Low-energy ion irradiation effects on chlorine desorption in plasma-enhanced atomic layer deposition (PEALD) for silicon nitride," Jpn. J. Appl. Phys. 61, SI1011 (2022).

AF-MoP-34 Effect of Precursor Temperature of 1,4-Phenylene Diisocyanate (PPDI) on the Growth Rate of Polyurea Using Molecular Layer Deposition (MLD), ***Jae Seok Lee,*** *S. Song, B. Choi,* Korea University, Republic of Korea

For molecular layer deposition (MLD), it is important to find a saturated pulse, purge time at a specific temperature. In the case of a precursor in a solid state at room temperature, the vapor pressure is lower than that in a liquid or gaseous state, and thus a longer pulse, purge time is required. Since the vapor pressure of the precursor is proportional to the temperature, heating precursor during deposition can reduce the cycle time. However, for certain molecules, intermolecular dimerization occurring at temperatures above the melting temperature (T_m) may affect the growth rate of the thin film. Therefore, it is necessary to consider this and determine the appropriate precursor temperature.

In this study, MLD was used to synthesize a polyurea thin film using 1,4-phenylene diisocyanate (PPDI) and ethylenediamine (EDA) as precursors. 70℃, 120℃, and 180℃ are selected as precursor temperature based on T_m of PPDI which is approximately 99℃. Polyurea thin film was deposited on Si wafer at a room temperature. Growth per cycle (GPC) for each condition was measured using X-ray reflectometry (XRR) and Fourier transform infrared spectroscopy (FTIR) to evaluate the effect of PPDI temperature on the growth rate and structure of the thin film. In addition, to verify the dimerization of PPDI, heat treatment was performed at 70℃, 120℃ and 180℃ for a week using dry oven. Transition of PPDI molecular structure and physical properties were analyzed using differential scanning calorimetry (DSC) and FT-IR.

As a result, dimerization was identified at 120℃ and 180℃, which is the cause of the increasing melting point. Through XRR data, there is clear tendency of decrease in GPC with 120℃ and 180℃ cases while 70℃ does not. IR peak analysis is for double checking the results from PPDI. In conclusion, the precursor temperature must be decided considering both the reactivity and thermal stability of substances.

AF-MoP-35 Multicomponent $RuTiO_x$ Thin Films through Atomic Layer Modulation, *N. Trinh, C. Nguyen, B. Gu, H. Lee, **Mingyu Lee,*** Incheon National University, Republic of Korea

Recently, atomic layer deposition (ALD) has become a key technique for fabrication of multicomponent films in nanoscale devices. Conventionally, the supercycle method consisting of two or more ALD processes has been used, and the compositional ratio of the films can be controlled by cyclic ratio of two ALD processes. However, the compositional ratio often is not consistent with the theoretical calculation due to different surface reactions on each surface. Furthermore, the supercycle method requires a certain film thickness to maintain a compositional ratio, so it can't be used in a few nanometers thickness films. Based on understanding of surface reactions mechanism in atomic layer deposition (ALD), we have studied the concept of atomic layer modulation (ALM) for fabrication of the multicomponent thin film with atomic-scale control. The main key idea of ALM is that the compositional ratio is determined by the physical steric hindrance and the chemical reactivity of two precursors on the surface which can be predicted by theoretical calculations. We successfully fabricated a $RuTiO_x$ multicomponent thin film which have the potential applications for interconnects materials. The $RuTiO_x$ thin film was deposited with controllable dopant ratio using a Ru precursor, dicarbonyl-bis(5-methyl-2,4-hexane-diketonato)Ru(II) (Carish), and a Ti precursor, titanium tetraisopropoxide (TTIP). Due to the steric hindrance effect, the component ratio of $RuTiO_x$ thin films is determined by the exposure sequence of precursors. Theoretical calculations were employed using Monte Carlo (MC) and density functional theory (DFT) to study physical and chemical reaction mechanisms, respectively. The results are consistent with the experimental results analyzed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). With the ability to control doping concentrations even at atomic scale, not only the ALM method could be contributed to expand the possibility of fabricating multicomponent oxides materials, but also improving the quality of the deposited films.

AF-MoP-36 Fine-Tuning of Low Surface Energy Substrate Functionality to Lower the Nucleation Delay Inherent for ALD of Noble Metals, *S. Thalluri, R. Zazpe, J. Rodriguez-Pereira, H. Sopha, **Jan Macak,*** University of Pardubice, Czechia

Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance for various catalytic applications[1]. Due to their scarcity, efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique to facilitate lowering of loading mass on a support of interest[2],[3]. Furthermore, ALD is the most suitable technology that can decorate high aspect ratio and high surface area substrate architectures[4]. Due to the governing surface energy variations between noble metals and support surfaces, the growth initiates as nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. These variations are also known to increase the nucleation delay of noble metals especially for Ru considerably. In this regard our efforts were laid to improve the functionality with pretreatments on carbon paper (CP) supports which were shown promising to reduce the nucleation delay of ALD deposited Ru.

For electrocatalytic applications, it is important to choose the right substrates. Among available substrates, CP and titania nanotube (TNT) layers are best choices considering their physio-chemical properties, availability, vast literature, and low costs incurred using these as support substrates in electrocatalysis and photocatalysis. Several surface modifications for CP's and variations on morphological aspects of TNT layers had received a great attention form applied fields due to their improved surface area, conductivity and stability[5]–[8]. Uniformly decorating these CP's and TNT layers by NPs or thin films of catalysts proved

to be highly efficient with no boundaries on applications[9].

The presentation will introduce and describe the synthesis of different noble metal NPs by our ALD tool (Beneq TFS 200) on various aspect ratio TNT layers and CP substrates. It will also include the corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

References:

1. Huang, Z. F. et al. Advanced Energy Materials vol. 7 (2017) 1700544.

2. Yoo, J. E. et al. Electrochem. commun. 86, (2018) 6.

3. Anitha, V. C. et al. J. Catal. 365, (2018) 86.

4. Zazpe, R. et al. Langmuir 32, (2016) 10551.

5. Sopha, H. et al. Appl. Mater. Today 9, (2017) 104.

6. Macak, J. M., Zlamal, M., Krysa, J. & Schmuki, P. Small 3, (2007) 300.

7. Liu, C., Sun, C., Gao, Y., Lan, W. & Chen, S. ACS Omega 6, (2021) 19153.

8. Sitaramanjaneya M. Thalluri & Macak, J. M. Small 2023-Under Rev.

9. Dvorak, F. et al. Appl. Mater. Today 14, (2019) 1.

AF-MoP-37 Growth Behaviors and Structural Characterization of PEALD In_2O_3 thin films using Amide-based and Alkyl-Based Novel Indium Precursors*, **Gyeong Min Jeong**, Y. Kim, H. Yang,* Hanyang University, Republic of Korea*; M. Kim, S. Lee, Y. Kwone, S. Jeon, Y. Im,* DNF, Republic of Korea*; J. Park,* Hanyang University, Republic of Korea

Oxide semiconductors are attracting attention as active channel materials due to their advantages like high field effect mobility, low off current, and low process temperature. Indium-based oxides, such as In-Ga-Zn-O (IGZO), In-Ga-Sn-O (IGTO), In-Ga-O (IGO), have been mainly studied for high electrical characteristic. Indium oxide is critical source in electron properties because it has very low electron formation energy that can easily generate electron. Indium provides carrier transport path through overlap from the large size of their 5s orbital. As the device scaling down according to Moore's law need nanoscale controlling in process, the atomic layer deposition (ALD) is powerful method which can control film thickness in atomic scale and can control chemical composition. Since ALD process is based on self-limiting reaction nature, choice of precursor has significant influence on the properties of thin film. Many indium precursors ($InCl_3$, TMIn, InCp, DADI, In-CA-1, etc.) for ALD have been developed. Especially, (3-Dimethylaminopropyl) dimethylindium (DADI) is mostly used precursor in developing oxide semiconductor. The DADI precursor which is liquid phase has moderate GPC because amine ligand has high reactivity, but it is expensive and has low vapor pressure. In contrast, TMIn is inexpensive and high vapor pressure precursor than DADI, but it is a solid phase material that make low growth rate properties. So that, researching the cheaper precursor that have high reactivity and high growth rate is needed. In this study, we newly synthesized two indium precursors of DIP-3 and DIP-4 based on structure of DADI and TMIn, respectively. DIP-3 is liquid phase precursor based on DADI that have structure that is consist of amine ligand and coordination bond. On the other hand, DIP-4 is Alkyl based liquid phase material like TMIn. DIP-4 has not only higher vapor pressure compared to DIP-3 but also advantage in price. We made indium oxide film using DIP-3, DIP-4 and O_2 plasma in setting temperature 100 ~ 300°C. As a result, indium oxide layer using DIP-4 precursor has higher GPC (~1 Å/cycle) than DIP-3 (~0.6 Å/cycle). In addition, enlarged grains that help to enhance electrical properties are found from sample using DIP-4 due to smaller precursor size. We explain the origin of difference through analysis of film and DFT calculation. Therefore, it is useful method to get enhanced GPC and enlarged grain size that changing structure of precursor.

AF-MoP-38 Evaluation of a Zr Precursor and Hf Precursor with Higher Thermal Stability for the Atomic Layer Deposition of ZrO_2 and HfO_2 Films*, **Randall Higuchi,*** EMD Electronics*; R. Waldman, P. Arab, C. Chen, D. Lee,* EMD Electronics, USA

For DRAM applications the crystallinity of the dielectric film is critical to obtaining the correct dielectric constant. Precursors that allow higher temperature deposition could lead to crystalline as-deposited films and the thermal stability could lead to better step coverage. A Zr precursor and a Hf precursor were used to deposit ZrO2 and HfO2 films, respectively, in order to examine their deposition properties, electrical properties, and step coverage. These precursors have similar vapor pressure but improved thermal stability and can be deposited above 350C with no decomposition. Use of the Zr precursor with ozone shows a deposition rate of 0.65A.cyc from 250-350C. Use of the Hf precursor with ozone shows deposition rate of 0.65A/cyc from 300-350C. We looked at the leakage and EOT of the resulting ZrO2 and HfO2 films and showed comparable or better electrical performance to films deposited from other precursors. Crystallinity of the films was confirmed to correlate with the electrical performance. We also tested step coverage and the better thermal stability of the precursors led to improved step coverage. The current study covers the process window and electrical results for the investigated precursors.

AF-MoP-39 Hybrid PEALD/PEVCD Reactor Design for Depositing Thick GaN Films on Si*, **Birol Kuyel**, A. Alphonse, J. Marshall,* NANO-MASTER, Inc.

Depositing thick GaN on Si wafer using PECVD or CVD will require a thin buffer layer on sapphire wafers. We have presented results showingALD deposited GaN on Si wafer could possibly be a buffer layer for growing thick GaN layer on Si because of Si/GaN interlayer mixing* during ALD deposition. Now we want to show results of depositing a thick GaN film in a PECVD system on a Si wafer having ALD GaN. Furthermore we will show that our new “Hybrid PEALD/PECVD reactor”** can deposit both thin ALD buffer layer and thick PECVD GaN on Si wafer in same chamber without changing the hardware and breaking the vacuum.

*Deposition of GaN using $GaCl_3$ with N_2 plasma using PAALD, 44th ICMCTF conference at San Diego, Apr 2015.

**Patent US11087959B2

AF-MoP-41 ALD Infilling of Macroscopic Nanoporous Solids: Expanding Beyond Al_2O_3*, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

ALD of Al_2O_3 from trimethylaluminum (TMA) and water has many advantages as an infill process for macroscopic nanoporous solids. Both TMA and H_2O are relatively small molecules that diffuse relatively quickly through nanopores, and their excellent stability at ALD temperatures prevents decomposition during infiltration, which for macroscopic substrates can take several minutes regardless of molecule size. Additionally, the production of approximately 1.5 moles of methane for every mole of TMA consumed enables relatively straightforward monitoring of deposition progress with the ALD chamber pressure gauge. Many potential nanocomposite applications, however, require infills other than Al_2O_3 with specific optical, electronic, or chemical properties. In this work, we infill macroscopic (>1 mm thickness) nanoparticle networks (e.g., ~100 nm Al_2O_3 nanoparticles) with ZnO using diethylzinc (DEZ) and water or with SiO_2 using bis(t-butylamino)silane (BTBAS) and ozone, and we compare our results to those obtained from Al_2O_3 infilling. We explore strategies for achieving uniform and pure infills despite larger and less stable precursor molecules as well as methods for confirming infill completeness in the absence of obvious reaction/saturation signals in the chamber pressure readings. We determine infill uniformity and composition via analysis of nanocomposite mass and color as well as electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and electrical conductivity measurements.

AF-MoP-42 Properties of VHF PEALD Silicon Nitride Film Deposited by Precursors with Different Amino Ligands*, **Seung Yup Choi**, Y. Ji, H. Kim, J. Kang,* Sungkyunkwan University, Republic of Korea*; A. Ellingboe,* dublin City University, Ireland*; H. Chandra,* EMD Electronics*; C. Lee,* EMD Electronics, Republic of Korea*; G. Yeom,* sungkyunkwan University, Republic of Korea

Silicon nitride film is widely used in semiconductor and display industry as gate spacer and encapsulation layer, etc. Among various deposition methods, plasma enhanced atomic layer deposition (PEALD) methods using Si precursor with nitrogen plasma are attracting attention due to advantage of low temperature deposition in addition to excellent thickness control, conformality, etc. as the ALD method. Among different Si precursors for silicon nitride PEALD, chlorosilane precursors commonly used in PEALD processes have corrosive reactants and particle issues for their byproducts. Amino silane precursors, compared to chlorosilane, can be used for lower temperature deposition but film conformality using aminosilane with N_2 plasma is known to be one of the biggest challenges. In this study, to overcome such challenge, two amino silane precursors with different types of ligands were studied for SiN x thin film properties deposited by PEALD

using N_2 plasma excited by very high frequency (VHF, 162MHz). Compared to BTBAS having two amino ligands, DSBAS having one amino ligand showed prominent film properties. Silicon nitride thin film grown by DSBAS showed smoother surface, higher density, higher breakdown field, lower wet etch rate and higher growth per cycle (GPC) than BTBAS due to its structural feature. Furthermore, the fact that DSBAS films at 300℃ has less impurities such as carbon was revealed through XPS analysis. Also, DSBAS exhibited remarkable step coverage when deposited on high aspect ratio (30:1) trench pattern at 300℃.

AF-MoP-43 Influence of Metal Precursors on the Low-Temperature Crystalline Vanadium Oxide Synthesis Using Oxygen Plasmas*, A. Mohammad, K. Joshi, D. Rana, S. Ilhom, B. Wells, B. Sinkovic,* University of Connecticut*; A. Okyay,* Stanford University*; **Necmi Biyikli**,* University of Connecticut

Vanadium oxide shows phase-change behaviors at different stoichiometries including the metal-insulator transition (MIT) for VO_2around 70 °C shifting between monoclinic to tetragonal rutile structure phase. Such materials have the potential to be used in low power opto-electrical switches and in memory devices. The ALD reports in the literature show VO_x growth mainly via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant and the as-grown VO_x films are mostly amorphous. Post-deposition thermal annealing at comparatively elevated temperature (typically higher than 500 °C) is performed to transform the as-grown amorphous films to different crystalline structures. However, no significant report is yet noticed on low-temperature as-grown crystalline VO_x films grown by thermal or plasma-ALD.

Our aim in this work is to demonstrate as-grown crystalline VO_x films using a hollow-cathode plasma HCP-ALD reactor at substrate temperatures 150 °C and to further improve the crystalline quality and transform the phase structure of the deposited VO_x film into the desired VO_2 stoichiometry. We have grown crystalline V_2O_5 thin films at 150 °C using TEMAV as the vanadium precursor and O_2 plasma as the oxygen co-reactant. The recipe for the plasma-ALD experiments was as the following: 0.250 s of TEMAV pulse with 10 sccm of N_2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O_2 plasma for 10 s, plasma power 50- 300 W, followed by another 10 s of Ar purge. The TEMAV precursor cylinder is heated at 115 °C to provide enough TEMAV precursor in the reactor. The resulting films are crystalline V_2O_5 with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

We have also experimented the VTIP precursor grown vanadium oxide thin films via HCP-ALD process (with 0.09 s dose and heated at 60 °C) under the same plasma parameters and substrate temperature. The as-grown film is still V_2O_5 with a refractive index ~2.55. While comparing the VO_x films grown by TEMAV and VTIP precursor, it was noticed that TEMAV experiments resulted in higher GPC compared to the VTIP experiments. We have performed post-deposition thermal annealing and were able to obtain VO_2 phase at 500 °C.

We will present a detailed optical, structural, and electrical characterizations to explore both the similarities and differences between the TEMAV and VTIP metal organic precursor grown VO_x thin films.

AF-MoP-47 Characterizing TEMAZ and TBTEMT for ALD*, **Marjorie Sarad**, J. Daubert, K. Cheatham, T. Adam, J. Kelliher,* Northrop Grumman

In this work, we studied the atomic layer deposition of ZrO2 and Ta2O5 using Tetrakis(ethylmethylamino)Zirconium (IV) (TEMAZr) and (tert-butylimido) tris(ethylmethylamido) Tantalum (V) (TBTEMTa) respectively with water as an alternative to Tetrakis(dimethylamido)zirconium(IV) (TDMAZr)and Tris(diethylamido)(tert-butylimido)tantalum(V) (TBTDETa). The new precursors were evaluated because they offer higher thermal stability than the existing precursors. These precursors offer a lower vapor pressure which produce films properties that were similar. We explored the deposition rate of ALD ZrO2 and Ta2O5 in the temperature range of 80℃ - 200℃ which produced amorphous films. We report on the film properties of deposited and annealed films as measured by ellipsometry, X-ray diffractometer and Toho 2320-S stress gauge. The films were annealed to determine a change in roughness and establish temperature the film changes to polycrystalline. We investigated the wet etch rate for both BOE and HF, and how those changes with annealing. Metal Insulator Metal capacitors (MIMCAPs) were built to measure the films' electrical properties in terms of capacitance, leakage, and breakdown voltage were measured and evaluated after forming gas anneal for a 300 Å film. The dielectric constant was calculated from the capacitance-voltage measurement.

The ZrO2 film deposited by wither precursor TEMAZ or TDMAZ behaves similar, both crystallizes at 300℃ and neither deposited film etches with HF. The ZrO2 film, however, does etch with BOE and a linear decrease on the etch rate is measured when deposited at higher temperature. Films deposited at 80℃ and 120℃ had no change in stress after annealing, but the stress of the 200℃ deposited film became twice as tensile after annealing.

The TBTEMTa precursor achieved enough vapor pressure at 125℃ for uniform deposition from 80℃ to 200℃. The TBTDETa precursor needed the boost system to get sufficient vapor pressure at 120℃ for a uniform film. Both old and new precursor did not show any film removal with BOE. At lower processing temperature, Ta2O5 easily etches with HF. However once furnace annealed at 750℃ for an hour, the etch rate decreases by 30% and we report on the WER and stress. The films deposited at 80℃ had a density change after a 750℃ anneal for an hour, and the stress becomes more tensile after further annealing of the film. The Ta2O5 films deposited at 120℃ and 200℃ deposition had no change in density even after 5hr at 750℃, but the stress becomes more compressive. We will compare the effects of rapid thermal annealing (RTA) with shorter time against diffusion furnace anneal.

AF-MoP-48 ALD Film Closure and Thickness by Low Energy Ion Scattering*, R. ter Veen, **Karsten Lamann**, M. Fartmann, B. Hagenhoff,* Tascon, Germany

The applications of ALD have continuously been expanding. Whereas this deposition technique was initially focusing on the manufacturing of thin films for semiconductor applications on flat samples, currently ALD is used in a variety of fields, with many different substrate topologies. ALD has been used amongst others to manufacture pillar structures, to deposit metals on catalyst supports with high specific surface area, and in the application of coatings to protect cathode materials in Li ion batteries.

When the applications of ALD are expanding, characterization techniques need to follow this trend. Low Energy Ion Scattering (LEIS) does this. LEIS is a chemical analysis technique that is specific to the outermost atomic layer on a sample, making it the most surface specific chemical analysis technique in existence. This makes it particularly suited to determine film closure. The one monolayer specificity gives LEIS a distinct advantage in the determination of film closure over other techniques (e.g. ellipsometry, XRF). These other techniques can determine how much is deposited, but cannot tell the difference between one closed layer and a half closed double layer.

The presentation will first reporton LEIS applications to thin films deposited on flat samples (the nucleation behavior of GaSb films on SiO_x, figure 1). The second part of the presentation will focus on expanding the applicational range of LEIS to thin films on rough materials and particles with a chemically more complex composition. Samples are taken from cathode material for Li ion batteries, in particular, AlO_x films deposited on $LiMnNiCoO_x$ (figure 2).

AF-MoP-49 Development of HF-Free YF3 ALD Process and Its Dry Etch Resistance*, **Sunao Kamimura**, T. Teramoto,* Air Liquide Laboratories, Japan*; T. Ono,* Air Liquide Advanced Materials*; C. Dussarrat,* Air Liquide Laboratories, Japan*; N. Blasco,* Air Liquide Advanced Materials, France*; N. Gosset,* Air Liquide Laboratories, Japan*; G. Nikiforov,* Air Liquide Advanced Materials

Aluminum-based ceramics have been extensively used in semiconductor plasma processing equipment as plasma-facing materials. However, these materials are eroded by corrosive fluorocarbon plasmas, resulting in the production of contaminant particles on the wafer. In order to solve this problem, yttrium oxide (Y_2O_3) and yttrium fluoride (YF_3) coatings have recently attracted substantial attention due to their high resistance to erosion in plasma, especially plasma etch, avoiding the generation of fluoride particles from the chamber wall surface, thereby reducing particulate contamination.

Atomic layer deposition (ALD) is a thin film coating method that enables conformal dense and pinhole-free film deposition even for the complex structures like showerheads. However, the formation of YF_3 thin films by ALD has been challenging since common fluorine sources such as HF are generally dangerous and corrosive, hence could lead to permanent damage to the chamber of semiconductor plasma processing equipment.

We have carried out the screening of several types of organometallic yttrium precursors for ALD, and have succeeded in depositing an ALD YF_3 film using a novel F containing yttrium organometallic precursor called

Ybeta-prime in combination with O_3 as the co-reactant. These precursors are introduced sequentially, leading to a HF-free YF_3 thin film coating process. The YF_3 thin film growth was confirmed by XPS measurements, and it revealed that growth per cycle (GPC) increases as reactor temperature increases. The refractive index of deposited YF3 thin film was constant with the deposition temperature, its value being consistent with bulk YF_3 value. Dense, uniform, conformal hydrophobic (WCA > 90 degrees) films are obtained at the range of temperature between 225ºC and 300ºC. SEM was used to measure step coverage of the ALD YF_3 film deposited at 275ºC in a 1:6.25 aspect ratio structure. The SEM image shows excellent step coverage (top: 22 nm/bottom: 22 nm), opening interesting perspectives for industrial applications requiring high conformality. This contrasts with YF_3 films obtained through CVD processes.

The erosion behavior of YF_3 coupon was analyzed under representative plasma etching conditions, using the same bias power and processing gases (CF_4 and O_2) where high density CF_4/O_2 plasma are produced (RF source power: 1300 W. RF bias power: 200 W). Etch rates of YF_3 thin film was one order of magnitude lower than Al_2O_3 thin film. Furthermore, Y_2O_3 thin film prepared using an ALD technique was used to compare the surface erosion behaviors with YF_3 film.

We are uncovering a new class of HF-free metal fluoride processes that go well beyond yttrium.

AF-MoP-50 Role of Ga Doping in IZO Films Grown by Atomic Layer Deposition*, **Ae-Rim Choi**, I. Oh, Y. Jeong, D. Lim,* Ajou University, Republic of Korea*; S. Kim, S. Ryu, D. Kim,* SK Hynix, Korea

Recently, DRAM devices have faced physical limitations of scaling down, involving inhigh leakage current. Thin film transistor (TFT) with a indium-based multi-component oxide semiconductor has been suggested to replace conventional 1T1C DRAM structure. For example, InZnO (IZO) films have high field-effect mobility, optical transparency, high conductivity, andhigh mobility.[1,3] Further,Ga doping into IZO films improves electrical properties.[4] Ga–O bonds, which are stronger than Zn–Oand In–O bonds, improve the controllability of carrierdensities in the nearly degenerate state.[5] However,in spite of its technical importance, the role of Ga doping has not been clearly unveiled. It would be because the lack of a proper fabrication method. Since doping concentration significantly affects electrical properties,4] the study of Ga-doped IZO films with deposition technique for precise controlling of chemical composition needs more attention.

Because of excellent conformality and thickness control, atomic layer deposition (ALD) is suitable for thin film deposition on complex nanostructures. In this work, we investigate ALD IZO films with gradual change of Ga contents, to elucidate the role of Ga doping. For the fabrication of Ga-doped IZO films, we employ super cycles consisting of multiple sequential steps of In_2O_3, Ga_2O_3, and ZnO, by $(CH_3)_2In(CH_2)_3N(CH_3)_2$, $Ga(CH_3)$, and $(C_2H_5)_2Zn$ precursors, respectively. The chemical composition is investigated by X-ray photoelectron spectroscopy (XPS). Grazing incidence X-ray diffraction (GI-XRD) is performed to study the crystallinity. Transmission electron microscopy (TEM) is also performed for interfacial analysis between gate insulator and channel layer and between channel layer and metal. TFT devices are fabricated by photolithography and the electrical properties of I_d-V_g curves are measured using B1500A semiconductor analyzer. We compare the performance of ALD IZO TFT devices with gradual increase of Ga doping and discuss the availability for next generation 3D DRAM devices.

[1] A. Belmonte et al, IEEE International Electron Devices Meeting (IEDM), (2020)

[2] H.-J. Ryoo. et al, Nanotechnology 32 (2021)

[3] K. Makise et al, J. Appl. Phys. 116 (2014)

[4] T. Yoshikawa et al, Appl. Phys. Express, 6 (2013)

[5] J. H. Lim et al, Scientific Reports, 7 (2017)

AF-MoP-51 The Effects of in-situ Atomic Layer Annealing on Thermal Atomic Layer Deposited Silicon Nitride*, D. Le, S. Hwang, J. Kim,* University of Texas at Dallas*; J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas*; M. Benham,* RASIRC*; **Si-Un Song**,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea

We demonstrated the deposition of thermal ALD SiNx over a wide range of deposition temperatures using anhydrous hydrazine (N2H4) as the nitrogen source.1 Although the N2H4–based process was able to deliver highly conformal thin films with an enhanced growth rate and improved film properties compared to ammonia (NH3), the wet etch resistance was still undesirable.

Herein, we examined the impact of the in-situ atomic layer annealing (ALA) process utilizing Ar plasma on thermal ALD silicon nitride (SiNx) thin films. The growth characteristics, wet-etch rate (WER), bonding information, and conformality over different aspect ratio (AR) nanotreches of the SiNx with in-situ plasma cycles were carefully investigated and compared to the reference process (thermal ALD only).

When the in-situ plasma treatment was introduced in the thermal ALD process, the growth rate of SiNx was reduced by ~45% compared to the standard procedure. While SiNx deposited via the standard ALD process exhibited a growth rate of ~0.05 nm/ cycle, the ALD/ALA process delivered thin films with a growth per cycle (GPC) of ~0.022 nm/ cycle between 320–480 °C. Despite the decrease in growth rate, the addition of in-situ ALA treatment resulted in notable enhancements in the deposited SiNx thin film properties, such as improved reflective index (RI), lower wet etch rate (WER,) and increase in film density. At 410 °C, the RI increased from 1.80 to 2.00, suggesting thin films achieved with ALD/ALA process would be more Si-rich than thermal-ALD. Furthermore, while the WER of SiNx decreased from 12.9 nm/ min to 0.69 nm/min (evaluated in diluted HF 200:1), the film density increased from 2.61 to 2.80 g/ cm3. Ex-situ FTIR was employed to further investigate the effects of in-situ atomic layer annealing on embedded –NHx (x=1,2) bonds within the deposited thin films. Compared to the reference sample, the thin films that deposited with the additional plasma cycles showed a slightly lower –NHx bond density. Furthermore, the conformality of ALD/ALA SiNx thin films was also evaluated using ~6:1 AR trench structures. The TEM cross-sectional images showed >80% conformality of SiNx thin film could be achieved when incorporating the in-situ plasma treatment into the ALD process. The experimental details and results will be presented.

We would like to express our gratitude to RASIRC Inc. for their financial support and for providing BRUTE hydrazine source.

[1] ALD 2021, Paper Number: 69751.

AF-MoP-52 Low Toxicity Electron Transport Layer of Atomic Layer Deposited TiO_2 and SnO_2 for Sb_2S_3 Thin Film Solar Cells*, Y. Kim, P. Pawar, **Jaeyoung Heo**,* Chonnam National University, Republic of Korea

In antimony sulfide (Sb_2S_3) thin-film solar cells (TFSCs), the hole transport layer (HTL) is an important parameter to minimize interface defects at the Sb_2S_3/metal interface, thus providing better charge carrier extraction. However, HTL materials are highly expensive and toxic and demand a controlled atmosphere. In addition, they are susceptible to the humid environment, thus resulting in reduced performance. Recently, the application of double buffer layers has been proven to be a beneficial approach for the enhancement of the power conversion efficiency (PCE) of Sb_2S_3 TFSCs. Herein, atomic-layer-deposited (ALD) SnO_2 and TiO_2 ETLs were applied as a double buffer layer with CdS for Sb_2S_3 TFSCs. The Sb_2S_3 absorber was deposited using a facile hydrothermal method. The TFSC devices were fabricated based on FTO/SnO_2/CdS/Sb_2S_3/Au or FTO/TiO_2/CdS/ Sb_2S_3/Au structure without HTLs. Experimental analysis revealed the reduction of the surface roughness of ETLs and decreased unfavorable (hk0) orientation of the Sb_2S_3 absorber after utilizing double buffer layers. Initially, incomplete nucleation of Sb_2S_3 was observed on SnO_2 and TiO_2 ETLs, which resulted in the formation of a shunting path. Conversely, complete nucleation of Sb_2S_3 was observed on CdS and double buffer layers. The highest PCEs of 3.98% and 4.23% were obtained for SnO_2/CdS and TiO_2/CdS double-buffer-layer-based cells with improvements exceeding 1% compared with the reference CdS buffer layer. Additionally, improvements in open-circuit voltage (V_{OC}) of the order of ~25 mV and ~45 mV were respectively observed for SnO_2/CdS (V_{OC} = 0.676 V) and TiO_2/CdS (V_{OC} = 0.696 V) double-buffer-layer-based devices compared with the reference CdS buffer layer (V_{OC} = 0.648 V). The enhanced device properties are mainly attributed to the improved charge carrier collection and formation of suitable band offset at the absorber and ETLs interfaces.

AF-MoP-53 Growth and Crystallization of Conductive srruo3 Films by Atomic Layer Deposition Depending on the Substrates*, **Youngsin Kim**, C. Hwang,* Seoul National University, South Korea

This study reported the properties of SrRuO3 (SRO) thin films used as bottom electrodes of SrTiO3 (STO) dielectric films. The SRO has a close

lattice match with the STO, making it a suitable electrode for STO crystallization.[1] The SRO films were grown via atomic layer deposition of SrO and RuO2 using Sr(iPr3Cp)2 and Rudense® as precursors, respectively, on different substrates. It was confirmed that the growth rate of RuO2 using the Rudense® precursor is relatively lower during the SRO deposition process compared to the conventional RuO2 deposition with the pulsed chemical vapor method using the ToRuS as the precursor.[2] Unlike the SRO films grown with ToRuS, which showed excessive RuO2 growth due to the catalytic characteristic of the intermediate metallic Ru, the SRO films grown with the Rudense® precursor did not show undesirable excessive growth since the catalytic effect was not involved.

The SRO films were crystallized with rapid thermal annealing (RTA) at 650oC in an O2 atmosphere after deposition. TiN, Pt, Si, and Al2O3 substrates were used to deposit the SRO. The atomic force microscopy (AFM) analysis (Figure 1) revealed that the surface roughness was highest and lowest when TiN and Al2O3, respectively, were used as the substrate. The SRO films deposited on the TiN substrate showed cracks on the surface when observed by the scanning electron microscope (SEM). In addition, the sheet resistance of the SRO sample deposited on the TiN substrate, measured by the 4-point probe, was about 100 times higher than samples using other substrates. The SRO peak was not observed with the grazing incidence X-ray diffraction (GIXRD) when Pt was used as the substrate. The SRO peak was only observed by GIXRD when the oxygen partial pressure was increased by more than 7 times. The transmission electron microscope (TEM) of the SRO film deposited on the Pt substrate revealed that the film was amorphous, although the aggregation characteristics were observed. It is presumed that the Pt crystal trapped the oxygen needed for the SRO growth, which suppressed the formation of the crystallized SRO.

References

[1] J. W. Han et al., "Growth of Conductive SrRuO3 Films by Combining Atomic Layer Deposited SrO and Chemical Vapor Deposited RuO2 Layers," Chemistry of Materials, vol. 24, no. 24, pp. 4686–4692, Dec. 2012

[2] D. Y. Kwon et al., "Atomic layer deposition of Ru thin films using (2,4-dimethyloxopentadienyl)(ethylcyclopentadienyl)Ru and the effect of ammonia treatment during the deposition," Journal of Materials Chemistry C, vol. 8, no. 21, pp. 6993–7004, Jun. 2020

AF-MoP-54 In-Situ Gas Monitoring of ALD Processes Using Remote Optical Emission Spectroscopy*, **Nessima Kaabeche**, Gencoa, UK; C. Guerra,* Swiss Cluster, Switzerland*; J. Brindley, D. Monaghan,* Gencoa, UK

Effective and robust monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behaviour as well as being an important step in the eventual wide-spread industrialisation of the ALD technique.

Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is not often undertaken, especially at the production stage.

An alternative gas sensing technique that operates directly at pressures above 10^{-4} mbar has been built around remote plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor's plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species. Importantly, this plasma, generated inside the sensor, has a sole function as a gas detector and does not affect the ALD process itself.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Previous work had demonstrated the usefulness of this technique, but limitations were encountered when using a DC voltage to generate the sensor's plasma as contamination and reduced sensitivity developed when used with certain precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. It will be demonstrated that the pulsed power technique is more effective than DC in preventing contamination of the sensor's electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products.

Examples of this sensing technique's practical uses for Al_2O_3 processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

AF-MoP-55 The Application of Rare-Earth Metals as ALD Precursors*, **Yu-Chieh Pao**,* Industrial Technology Research Institute, Taiwan*; B. Lee,* Industrial Technology Research Insitute, Taiwan

Rare-earth metal compounds have exquisitely unique electronic and magnetic properties that make them irreplaceable in the field of semiconductor, manufacturing, chemical industry, etc. As the technology trend is focused towards downscaling the size of transistors, rare earth oxides are becoming increasingly important in the field of microelectronics due to large band gaps, high dielectric constants, and good thermodynamic stability on silicon. Therefore, rare-earth metal oxides such as La2O3 can be utilized as the gate dielectric layer in field effect transistors.

The advantages of atomic layer deposition (ALD) such as high conformality, high uniformity, and precise thickness control, are all important when trying to downscale the size of transistors. As a result, the development of ALD precursors HAS attracted much attention. From a molecular design point of view, by selecting the appropriate type of ligand and modifying the substituent group of ligands, properties such as thermal stability, vaporization rate, reactivity and purity of resulting thin film can be readily adjusted. The design and application of rare-earth element-related ALD precursors will be introduced in this paper.

AF-MoP-57 Characterization of Snox Thin Films Deposited by Atomic Layer Deposition*, **Taekjib Choi**, S. Lee, J. Yun,* Sejong University, Republic of Korea*; I. Choi, B. Cho, J. Yang,* TES Co., Ltd., Republic of Korea

Metal oxide photoresists are currently being considered as alternatives to chemically amplified resists. They consist of a metal oxide core surrounded by ligands that tune solubility, crosslinking and other properties and provide high etch resistance. In particular, organotin compounds are highly sensitive to extreme ultraviolet (EUV), enabling high-resolution patterning. The strength and dissociation mechanism of C-Sn bonds are factors that can be related to EUV photosensitivity. And SnO_x photoresists are presented as EUV resist with high absorptivity and etch resistance. SnO_x thin films deposited by TALD and PEALD were compared under different deposition temperatures. We analyzed the optical, chemical, and electrical properties of the SnOx thin films under various deposition conditions, focusing on the influence of the carbon ratio. Additionally, we will evaluate and discuss their etch properties.

AF-MoP-58 Laser Diagnostics of Plasma Surface Interactions*, **Mruthunjaya Uddi**,* Advanced Cooling Technologies*; A. Dogariu,* Texas A&M University*; E. Kudlanov,* Advanced Cooling Technologies*; G. Urdaneta,* texas A&M University*; Y. Xiao, D. Jensen, C. Chen,* Advanced Cooling Technologies

Plasma surface interaction has been a critical area of research for many applications such as Plasma-Enhanced Atomic Layer Deposition (PEALD). To meet the demanding needs of more advanced atomically controlled microfabrication methods, the physics of PEALD needs to be better understood to enable high quality, repeatable and controllable deposition process. Several challenges that need to be addressed regarding PEALD include damage to the substrate from highly energetic species and UV radiation, need for precise amorphous/crystalline modulated selective layer deposition, conformality in coating non-uniform substrates, achieving an aspect ratio of >100, repeatability and controllability of the finish. To address these challenges, we are developing laser diagnostics methods to measure species over substrates by advanced laser diagnostics such as femtosecond- Two-Photon Absorption Laser Induced Fluorescence (fs-TALIF) to image N atoms over substrates. Here we present measurements of N atom densities over a substrate with high spatial (< 10 microns) and time resolution (<1 ns) using fs-TALIF at pressures of 5-150 mTorr.

AF-MoP-59 Density-Functional Theory Modeling for Thermal Atomic Layer Etching of Cobalt with Hexafluoroacetylacetone Chelation*, S. Chae, **Sangheon Lee**,* Ewha Womans University, Republic of Korea

In this study, a thermal atomic layer etching process for Co comprising two steps—plasma chlorination and chelation with hexafluoroacetylacetone (Hhfac)—was developed. We investigated the thermodynamics associated

with the adsorption of Hhfac on chlorinated Co surfaces, and the subsequent removal of these surfaces based on the disk-like $CoCl_2$ models. We employed a disk-like chlorinated Co surface model and identified thermodynamically favorable reaction pathways and governing factors controlling the overall etching process. We found that thermodynamically the most favorable reaction pathway proceeded via the adsorption of hfac on a low-coordinated surface Co site followed by the desorption of $CoCl_2$hfac cluster; the adsorption and desorption steps were thermodynamically uphill and downhill, respectively. We also found that the kinetic energy barrier for the Hhfac adsorption step tended to be noticeably greater than that for the $CoCl_x(hfac)_y$ desorption step. These calculation results suggest that the Hhfac adsorption step is the rate-determining-step in the chelation process of chlorinated cobalt surfaces. Finally, we suggest that the strong tendency of the hfac-induced sp^3 hybridization of Co is a governing factor in the thermodynamics of etching the chlorinated Co layer with Hhfac as an etching gas.

AF-MoP-60 Study on Phase and Chemical Bonding of Molybdenum Film Grown by Atomic Layer Deposition*, **So Young Kim**, C. Jo, H. Shin,* Yonsei University, Republic of Korea*; M. Cheon, K. Lee, D. Seo, J. Choi,* Hanwha Corporation, Republic of Korea*; H. Park,* BIO-IT Micro Fab Center, Republic of Korea*; D. Ko,* Yonsei University, Republic of Korea

As the semiconductor integration has advanced, there have been limitations in selecting candidates for interconnect metals because of the exponential increase in metal resistivity at scaled pitches. Tungsten and copper are the most widely used materials for back-end contact vias and metal lines. However, their resistivity increases up to ~19[1)] and ~22 μΩcm[2)] at 10 nm thick film while their bulk resistivity are as low as 5.28 and 1.67 μΩcm, respectively. Therefore, there are needs for finding metals with lower resistivity for contact and back-end metal at tight pitch, which has led to the emergence of molybdenum, cobalt, and ruthenium as promising alternatives over traditional metals. Among those next generation metals, molybdenum has the lowest product of electrical resistance and electron mean free path($\rho o \times \lambda$)[3)]; it has a merit of having low resistivity, compared to copper and tungsten, as thickness reduces.

Since molybdenum film grown by atomic layer deposition(ALD) has not yet been actively studied, we investigated the phase and chemical bonding states of molybdenum film at different thickness. We also examined the feasibility of molybdenum nitride as the diffusion barrier of molybdenum against silicon oxide. Molybdenum films and molybdenum nitride films were deposited by thermal ALD equipment, manufactured by Hanwha Corporation, using MoO_2Cl_2 precursor as molybdenum source and H_2 and NH_3 as reducing agent.

The phases of molybdenum were observed by grazing incidence x-ray diffraction(GIXRD) and the morphology and surface roughness of the thin films were observed by atomic force microscope(AFM). X-ray Photoelectron Spectroscopy(XPS) showed the Mo concentration and binding energy of the film. The sheet resistance obtained by 4-point-probe(4PP) and the thickness measured by X-Ray Reflectometry(XRR) were used to calculate the resistivity of the Mo film. The phase and binding energies were analyzed via GIXRD and XPS to confirm the successful growth of pure Mo film. As-deposited 10 nm-thick Mo film showed standard XRD peaks for polycrystalline-Mo phase. In addition, ALD-grown Mo films showed low resistivity of ~13 μΩcm with 10 nm thickness while it increases up to ~30 μΩcm when the film thickness become as low as 6 nm.

1) D. Choi, B. Wang, S. Chung, X. Liu, A. Darbal, A. Wise, N. T. Nuhfer, K. Barmak, A. P. Warren, K. R. Coffey and M. F. Toney, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 29 [5], 051512 (2011).

2) J. W. Lim and M. Isshiki, J. Appl. Phys. [DOI:10.1063/1.2194247].

3) D. Gall, J. Appl. Phys. 119 [8], 1 (2016).

AF-MoP-61 Area-Selective Atomic Layer Deposition of Silicon Nitride for Nand Flash Memory with a Very High-Frequency Plasma Source*, **Min-Jeong Rhee**,* Ajou University, Republic of Korea*; W. Lee,* Pukyong National University, Republic of Korea*; I. Oh,* Ajou University, Republic of Korea*; G. Yoo,* Soongsil University, Seoul, Republic of Korea*; J. Heo,* Ajou University, Suwon, Republic of Korea

Silicon nitride (SiN_x) thin film has been used as a charge trap layer (CTL) in 3D NAND flash memory devices. Because thermal atomic layer deposition (ALD) demands a relatively high temperature, SiN_x is mostly deposited via the plasma enhanced-ALD (PE-ALD) technique for low impurity contents. However, due to energetic radicals in plasma, PE-ALD usually produces low step coverage and bottom layer damage. In NAND flash memory, damage to the SiN_x of the bottom layer can lead to tunnel oxide degradation and a reliability problem. Therefore, the development of a SiN_x process with high step coverage and low damage to the bottom substrate while maintaining the advantages of a low deposition temperature is required. In addition, in scaled 3D NAND flash devices, the isolation of each CTLs is required for device reliability by reducing cell-to-cell interference. However, the conventional top-down photolithography cannot achieve topological the formation of patterns or selective growth of thin films, where patterned films should be grown vertically separated on the tunnel oxides.

In this study, we develop the area selective ALD (AS-ALD) process of SiN_x films through very high frequency (VHF) plasma. We used bis-diethylamino silane ($H_2Si((N(C_2H_5)_2)_2)$) as a precursor and N_2 plasma as a reactant. The process using radio frequency (RF, 13.56 MHz) will be comparatively discussed with that using VHF, 60 MHz by chemical composition, step coverage, and damage of the thin film through X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). For AS-ALD, the inhibitors are sequentially deposited prior to each PE-ALD cycle, and the selectivity of each cycle was calculated. For a more accurate selectivity analysis, the selectivity between the metal substrate and the oxide substrate was analyzed through TEM. This comparative research and the AS-ALD process of SiN_x show the applicability of VHF PE-ALD in NAND flash memory, which requires high step coverage, low damage, and high capacity.

AF-MoP-62 Growth Mechanism of Ge-Sb-Te Thin Films by Supercycles of ALD GeTe and Sb_2Te_3*, **Okhyeon Kim**, Y. Kim,* Sejong University, Republic of Korea*; H. Kim,* sejong University, Republic of Korea*; C. Park, D. Ahn, B. Kuh,* Samsung Electronics Co., Ltd., Republic of Korea*; W. Lee,* Sejong University, Republic of Korea

Recently, a three-dimensional vertical architecture has been proposed to increase the integration and productivity of phase-change random-access memory (PCRAM) devices. Atomic layer deposition (ALD)technology is essential to prepare memory and switching materials on a high-aspect-ratio hole pattern with uniform thickness and composition. Since the ALD of Ge-Sb-Te (GST) film was reported by supercycles of ALD of GeTe and Sb_2Te_3 using an alkylsilyl Te compound [1], various ALD supercycle processes were reported using alkylsilyl Te compounds. In the ALD supercycle process of GST, GeTe thin films should be grown on Sb_2Te_3 thin films, and Sb_2Te_3 thin films should be deposited on GeTe, which is significantly different from the case of continuous growth of GeTe or Sb_2Te_3 film [2]. Therefore, in this study, we investigated the growth behaviors of ALD GeTe and Sb_2Te_3 during the supercycle process. The in-situ quartz crystal microbalance (QCM) analysis expected a Ge-rich, Te-deficient composition of the $GeTe_{1-x}$ thin film grown on Sb_2Te_3 films. To produce a stoichiometric $Ge_2Sb_2Te_5$ thin film by supercycle process, we controlled the ratio of $GeTe_{1-x}$ and Sb_2Te_3 subcycles and then annealed the deposited film in a Te ambient. As a result, a high-density stoichiometric $Ge_2Sb_2Te_5$ thin film was produced on a high-aspect-ratio pattern with a uniform thickness and composition.

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 ^{1}H-, ^{13}C- and ^{31}P- NMR spectroscopy, and its molecular structure has been confirmed by x-ray crystallography. Its low-melting point (35 ^{o}C) makes it easy to handle and enables liquid delivery. Thermogravimetric analysis shows good volatility, with $T_{½}$ 173 ^{o}C and low residual mass. The thermal stress analysis showed that it is stable at 200 ^{o}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).

ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-TuM

Precursors and Processes II

Moderators: Dr. Paul Poodt, Holst Centre / TNO, Dr. Paul J. Ragogna, University of Western Ontario, Canada

11:00am **AF2-TuM-13 Influence of Plasma Species on the Growth Kinetics, Morphology, and Crystalline Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition**, ***Jeffrey Woodward,*** *D. Boris,* U.S. Naval Research Laboratory; *M. Johnson,* Huntington Ingalls Industries; *S. Walton, J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple N_2/Ar plasma rather than $N_2/Ar/H_2$ or NH_3/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and N_2/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film structural properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the N_2 and Ar gas flows into the inductively coupled plasma source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), and synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al.*, J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:15am **AF2-TuM-14 Towards Self-Limiting III-Nitride Epitaxy via Hollow-Cathode Nitrogen Plasmas**, *N. Ibrahimli, S. Ilhom, A. Mohammad, J. Grasso, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*; **Necmi Biyikli,*** University of Connecticut

Research efforts on low-temperature synthesis of crystalline GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, stainless-steel based hollow-cathode plasma (HCP) sources revealed highly (002) oriented polycrystalline GaN films on Si(100) substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, in this study, monocrystalline GaN films on sapphire substrates was achieved at temperatures as low as 240 ℃. In this presentation we share our experimental findings on the epitaxial growth efforts of the entire wide bandgap III-nitride binary compounds including GaN, AlN, InN, and BN using self-limiting HCP-ALD.

The films were deposited using metal-alkyl precursors (triethylgallium, trimethylaluminum, trimethylindium, and triethylboron) and various nitrogen plasmas (N_2/H_2, N_2-only, N_2/Ar, and N_2/H_2/Ar) as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed within 200 – 250 °C temperature and 100 – 200 W rf-power range. *In-situ* Ar-plasma annealing cycles were also employed to enhance the surface crystallization process. *In-situ* ellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and reaction byproducts in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness, growth-per-cycle (GPC), and optical properties of the films. When compared to reference films grown on Si(100) substrates, GPC values obtained for III-nitride films on sapphire substrates showed a notable increase.

For GaN samples, grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline films on Si(100) substrates while GaN/sapphire samples exhibited no crystal peaks at all. Rocking curve XRD scans displayed a strong single (002) peak, confirming the monocrystalline character of the GaN films on sapphire substrates. We attribute this improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, chamber pressure). Among the binary III-nitride compounds, InN and BN films showed highest and lowest GPC values, respectively. With further improvement in film properties, we aim to achieve device quality electrical properties that can be used for back-end-of-the-line (BEOL) transistor channel layers.

11:30am **AF2-TuM-15 Thermal Atomic Layer Deposition of Gallium Nitride at 150 - 300°C using Tris(dimethylamido)gallium Precursor and Hydrazine***,* ***Adam Bertuch,*** Veeco Instruments*; J. Casamento, J. Maria,* Pennsylvania State University

Gallium nitride (GaN) and its alloys with aluminum nitride (AlN) have established themselves as leaders in electronic and photonic devices for high frequency, high voltage, and harsh environment applications.[1] This is due to their ultra-wide bandgaps, heterojunction polarization induced free carriers with high mobility in the absence of chemical doping, large thermal conductivity, and high temperature stability.The promising physical properties of this material system are generally realized by plasma assisted techniques such as molecular beam epitaxy (MBE) or high temperature metal organic chemical vapor deposition (MOCVD) processes. Accordingly, there are significant opportunities for new device functionalities and heterogeneous integration in batch processing if crystalline GaN with low impurity (e.g., oxygen and carbon) concentrations can be realized in a low temperature, plasma free process.

In this work, GaN thin films were deposited using Tris(dimethylamido)gallium (CAS 57731-40-5) and hydrazine (N_2H_4) at temperatures from 150°C to 300°C using thermal Atomic Layer Deposition (ALD). At these temperatures the process is self-limiting, exhibiting ALD behavior and a uniform growth per cycle (GPC) throughout the process chamber. For compositional analysis, the GaN films were capped *in-situ* using ALD deposited AlN with Trimethylaluminum (TMA) and Hydrazine. The ALD deposition rate for the GaN film is large, ranging from 1.2 to 1.4 Å/cycle, while the AlN growth rate is determined to be 0.30 to 0.75 Å/cycle, as a function of increasing temperature.

Compositional analysis by Auger emission spectroscopy (AES) revealed oxygen and carbon concentrations less than 5 atomic % at 300°C deposition for both the GaN and AlN film stack; among the best reported values for deposition temperatures less than 400°C.[2] Initial findings with scanning electron microscopy (SEM) show smooth continuous surface morphologies for the deposition on silicon substrates. Composition, crystallinity via X-Ray Diffraction (XRD), and RMS roughness via X-Ray Reflectivity (XRR) will be analyzed as a function of growth temperature. These results present a promising step towards the development of low temperature, plasma-free GaN based thin films.

References

[1]*High-Frequency GaN Electronic Devices,* edited by P. Fay, D. Jena, and P. Maki (Springer, 2019).

[2] S. Banerjee et al. J. Phys. Chem. C **123**, 23214 (2019).

11:45am **AF2-TuM-16 Crystalline Gallium Nitride Deposition on SiO_2/Si by RF-Biased Atomic Layer Annealing***,* ***Ping-che Lee,*** *A. Mcleod,* Univ. of Cal., San Diego*; S. Ueda,* Materials Science and Engineering Program, Univ. of Cal., San Diego*; J. Spiegelman,* Rasirc*; R. Kanjolia, M. Moinpou,* EMD Electronics*; A. Kummel,* Department of Chemistry and Biochemistry, Univ. of Cal., San Diego

High-quality GaN deposition on Si substrates attracts attention due to its high heat capacity, and thermal conductivity [1]. However, a major problem of current GaN on Si techniques is that thermal shrinkage causing microcracks during >700 ℃ MOCVD process. Here, polycrystalline GaN with 40 nm thickness on Si substrates at 275 ℃ was deposited by using an atomic layer annealing (ALA) process. Inert gas plasma was directed by an RF substrate biasing to bombard the growth surface of the ALD-grown GaN. Surface defects were healed through either atom displacement or a collision cascade[2, 3]. This GaN film was transferred to a sputter chamber and employed as a template for AlN for heat spreaders. The record high thermal conductivity AlN sputtered film (1 um thick) obtained in this work benefited from this ALA GaN layer, which improved the crystallinity and decreased the phonon-defect scattering at the interface. Other film deposition techniques could also be integrated into this novel ALA GaN layer to design a promising heat spreader.

The GI-XRD measurements (Fig. 1(a)) were preformed to investigate the film crystallinity. In the non-substrate-biased ALA, a diffraction peak at 34.5 ˚ showed that even gentle ion bombardment at the end of each cycle mobilized the surface adatoms. All of the RF-biased conditions demonstrated narrower FWHM values (0.65 ˚, 0.58 ˚, and 0.51 ˚, respectively), meaning that ions with comparatively higher momentum more effectively crystallized the films; this was further confirmed by an increase in film density observed by XRR in Table. 1.

Sputtered AlN was deposited on ALA GaN film to increase the total film thickness for thermal conductivity measurements. Grain boundary analysis (Fig. 1(b)) indicated that both the template GaN layer and sputter AlN layer had an identical bamboo grain structure. Moreover, the nanobeam electron diffraction in (Fig. 1(c) and(d)) showed that the (0002) axis of bottom GaN coincided with the top sputter AlN, which further confirmed that polycrystalline GaN layer pinned the growth direction of sputtered AlN. The larger thermal conductivity measured by time-domain thermoreflectance (TDTR) confirmed the effectiveness of this low-temperature buffer layer to achieve a record high thermal conductivity AlN (120 W/m*K) with a thickness of 1 um (Fig. 2). This local domain epitaxy relationship at the interface played a crucial role in ensuring that phonon delivering heat along (0002) axis would be relative uninterrupted by phonon-defect scattering.

[1] J. Leitner et al., Thermo. Acta, 401, 2003, 169-173,

[2] W.H. Lee et al., Appl. Surf. Sci. 525, 2020, 146615

[3] S.T Ueda et al., J. Mater. Chem. C, 10, 2022, 5707

ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-TuA
Plasma ALD I

Moderators: Erwin Kessels, Eindhoven University of Technology, Netherlands, Prof. Christophe Vallee, SUNY POLY, Albany

1:30pm **AF1-TuA-1 Plasma Enhanced Atomic Layer Deposition of Silicon Carbonitride***, S. Johnson, T. Yang,* University of Texas at Austin*; J. Zhao, T. Iwao, C. Schlechte, J. Carroll, G. Blankemeyer, P. Ventzek,* Tokyo Electron America Inc.*,; J. Resasco, G. Hwang,* ***John Ekerdt,*** University of Texas at Austin

Conformal deposition of dielectrics is necessary for many applications, including as spacers for self-aligned multiple patterning and as charge trap layers in NAND memory features. Plasma enhanced atomic layer deposition (PEALD) of silicon nitride is promising for these applications. However, silicon nitride films deposited with this technique typically have low HF acid wet etch resistance, limiting its applications. Incorporating carbon into silicon nitride to form silicon carbonitride (SiCN) films can overcome this shortcoming by increasing wet etch resistance, but it also increases leakage currents. By incorporating small amounts of carbon to form silicon carbonitride films, a large increase in etch resistance can be achieved with only a small increase in leakage current. Finding a process that delivers a ternary component film with specific material properties is inherently complex as both stoichiometry and bonding nature need to be controlled through surface reactions. Managing the carbon content and nature of bonding within SiCN films is the focus of this talk.

We use PEALD to deposit silicon carbonitride by alternating a thermal exposure of a silicon derived single source precursor containing Si-N, Si-C, and N-C bonds at 100 °C and a plasma step as a model system for SiCN deposition. The precursor contains all the film components (Si:C:N). A plasma step creates a surface on which the precursor can chemisorb leading to ideal film formation. An experimental capacitively coupled RF plasma source is used to survey how different plasmas, including ammonia, hydrogen, nitrogen, and pure argon impact of the nature of chemisorption and film nature. Films were characterized using *in situ* Fourier transform infrared spectroscopy (FTIR) and *in situ* X-ray photoelectron spectroscopy (XPS).First principles simulations are used to assess the fundamental mechanisms at play.

FTIR measurements show the plasma type has a large effect on the carbon bonding (C-C, C-N, C=N, C≡N, and C-Si) and the carbon content.XPS measurements reveal ammonia plasma results in no carbon being incorporated into the films; however, hydrogen plasmas result in significant carbon incorporation. Nitrogen plasma assisted processes are characterized by high growth per cycle and very high concentrations of C≡N and C=N bonds. Multiplexing different plasma treatment steps allows the film stoichiometry and bonding nature to be tuned. The fundamental mechanism associated with surface/film chemistry control is discussed in terms of the role of plasma species removal and addition of important nitrogen and carbon containing ligands.

1:45pm **AF1-TuA-2 Boron-Carbon Thin Films Deposited via PE-ALD***,* ***Neil Richard Innis,*** *C. Marichy, C. Bousige, C. Journet,* Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, France

Boron carbide (B_xC) finds diverse applications due to its superior hardness, high neutron absorption, and semiconducting nature. The band gap for boron-rich B_xC films is known to increase with an increasing B:C ratio. Magnetron sputtering[1], and high temperature (≥ 1000 °C) chemical vapor deposition (CVD) are the conventional processes to obtain boron carbide thin films. CVD involves boron hydrides[1] or halides[2] as precursors along with dihydrogen or simple hydrocarbons. Such precursors come with challenges such as high toxicity and/or corrosive by-products. Furthermore, conformality and thickness control of these films is still a challenge. To overcome it, atomic layer deposition (ALD) appears as a technique of choice, however, B_xC has never been synthesized by this technique so far.

From triethylborane (TEB) and hydrogen gas (H_2) as precursors, amorphous B_xC thin films with atomic-level thickness control on Si 100 substrate using plasma-enhanced atomic layer deposition (PE-ALD) are successfully obtained. The use of hydrogen plasma to remove ethyl groups of TEB to deposit $B_xC$films at low substrate temperatures (≤ 200 °C) is demonstrated. It should be noted that in this process the expected by-products are non-toxic and non-corrosive.

Here, the influence of the deposition parameters on the film growth rate, composition and structure will be discussed. The ALD reaction temperature is being investigated between 150 °C and 250 °C alongside spectroscopic ellipsometry. Additionally, the pulse/purge of precursors is optimized to ensure a saturated self-limited surface reaction, and the role of H_2 concentration and plasma power in the composition and growth of the deposit is being explored.

In-situ optical emission spectrometry (OES) is also performed to detect and compare the intensity of hydrogen lines, and to look at species responsible for etching and deposition during the ALD cycle. The impact of plasma-activated hydrogen species (as a function of plasma power and H_2 concentration) on the morphology and B:C ratio of the deposits is preliminarily assessed via secondary electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Moreover, surface-sensitive quantification and bonding information are obtained via time-of-flight secondary-ion mass spectrometry (ToF-SIMS) and ex-situ x-ray photoelectron spectroscopy (XPS).

References:

1. Pascual et al., *Diamond and Related Materials***8**, 402–405 (1999).

1. Byun et al., *Nanostructured Materials***5**, 465–471 (1995).

1. Buzhinskij et al., *Fusion Engineering and Design***45**, 343–360 (1999).

2:00pm **AF1-TuA-3 SiO_2 Electron-Enhanced Atomic Layer Deposition (EE-ALD) at Low Temperature Using Disilane and Ozone or Water as Reactants***, J. Gertsch, Z. Sobell, A. Cavanagh,* University of Colorado Boulder*; H. Simka,* Samsung Semiconductor, Inc.*;* ***Steven George,*** University of Colorado Boulder

Electrons can enhance SiO_2 atomic layer deposition (ALD) at low temperature using disilane (Si_2H_6) and either ozone (O_3/O_2) or water (H_2O) as the reactants.SiO_2 electron-enhanced ALD (EE-ALD) was demonstrated at 35°C by exposing the sample to sequential electron, oxygen reactant, and Si_2H_6 exposures (see Figure 1). The reaction sequence was electron beam exposure for 3 s, purge for 5 s, O_3/O_2 or H_2O exposure at 0.5-1.0 Torr for 3 s, purge for 10 s, Si_2H_6 exposure at 100 mTorr for 1 s, and purge for 15 s. The electron exposure was an electron current of ~150 mA for 3 s. The electrons were produced by a hollow cathode plasma electron source operating with a grid bias of ~-300 V. These electrons could irradiate a sample area of ~2 cm x 2 cm.

In situ spectroscopic ellipsometry measurements determined that the SiO_2 EE-ALD films nucleated rapidly and deposited linearly versus number of EE-ALD cycles on silicon wafers (see Figure 2). The SiO_2 EE-ALD growth rate at 35°C was 0.89 Å/cycle using O_3 and 0.88 Å/cycle using H_2O. The SiO_2 growth rate was also self-limiting at higher electron and Si_2H_6 exposures. The SiO_2 EE-ALD films could be grown on conducting silicon wafers or insulating SiO_2 films. SiO_2 EE-ALD is believed to be possible on insulating SiO_2 films because the secondary electron yield for SiO_2 at electron energies of ~100-300 eV is greater than unity. Under these conditions, the SiO_2 film charges positive during electron exposure and then pulls back secondary electrons to maintain charge neutrality.

The SiO_2 EE-ALD films had properties that were comparable with thermal SiO_2 oxides. The refractive indices of the SiO_2 EE-ALD films were n = 1.44 ± 0.02 and equivalent to the refractive index of a wet thermal SiO_2 oxide film. Depth-profile x-ray photoelectron spectroscopy (XPS) revealed that the SiO_2 EE-ALD films were high quality with carbon atomic percent below the detection limit. Grazing incidence x-ray diffraction (GI-XRD) analysis determined that the SiO_2 EE-ALD films were amorphous. In addition, the SiO_2 EE-ALD films yielded etch rates in dilute buffered oxide etch solutions that were only slightly higher than the etch rate of a wet thermal SiO_2 oxide film. SiO_2 EE-ALD should be useful to deposit high quality SiO_2 films on insulating and conducting substrates for various applications at low temperatures.

2:15pm **AF1-TuA-4 ALD of Transition Metal Chalcogenide TaS_x Using TBTDMT Precursor and H_2S Plasma***, **Sanne Deijkers**, H. Thepass,* Eindhoven University of Technology, The Netherlands*; H. Sprey, J. Maes,* ASM Belgium*; E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

Tantalum sulfide (TaS_x) is a transition metal chalcogenide (TMC) with applications ranging from optical switches and Cu diffusion barriers to quantum dots [1–3]. Currently, synthesis of TaS_x is done by mechanical exfoliation, chemical vapor deposition, or sulfurization processes. These processes lack control over the growth, are performed at relatively high temperatures, and/or are not suitable for large-scale processing, in contrast to the synthesis method of atomic layer deposition (ALD).

In this study, we have developed a plasma-enhanced ALD process of TaS_x using tert-butyliminotrisdimethylaminotantalum (TBTDMT) as Ta precursor and an H_2S plasma as co-reactant. Our ALD process of TaS_x is the first to be reported in literature. Films of TaS_x were grown on thermal SiO_2 in an Oxford Instruments FlexALreactor equipped with a remote inductively coupled plasma source. Growth of the TaS_x films has been monitored with in situ spectroscopic ellipsometry and shows a linear growth at the temperature range 150-300°C. Evaluation of the precursor dose shows slight soft-saturating behavior, requiring relatively long precursor dose times (20 s). Furthermore, the plasma dose saturates after 10 s. The resulting growth per cycle (GPC) at 300°C is 1.2 Å.

The TaS_x films have been investigated by x-ray photoelectron spectroscopy (XPS), and the results show that ALD TaS_x films contain minor carbon contamination (< 2%), are only slightly oxidized and have a Ta:S ratio of 1:2.9. Furthermore, the films have been investigated by Raman spectroscopy, x-ray diffraction and scanning electron microscopy.

1. Perfetti, L. *et al.* Time evolution of the electronic structure of 1T-TaS2 through the insulator-metal transition. *Phys. Rev. Lett.***97**, 1–4 (2006).
2. Lo, C. L. *et al.* Enhancing Interconnect Reliability and Performance by Converting Tantalum to 2D Layered Tantalum Sulfide at Low Temperature. *Adv. Mater.***31**, 1–10 (2019).
3. Zhou, L. *et al.* Tantalum disulfide quantum dots: preparation, structure, and properties. *Nanoscale Res. Lett.***15**, 1–8 (2020).

2:30pm **AF1-TuA-5 High Deposition Rate NbN and TiN for Superconducting Resonators for Quantum Devices by PEALD***, **Louise Bailey**, D. Besprozvannyy,* Oxford Instruments Plasma Technology, UK*; R. Renzas,* Oxford Instruments Plasma Technology*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; M. Powell,* Oxford Instruments Plasma Technology, UK

In recent years, plasma ALD has become a relevant technique in the field of nanoscale fabrication, including high-volume manufacturing, due to its self-limiting precursor behaviour and low temperature operation regimes. ALD is often limited to ultra-thin films, however, due to slow deposition rates. High-rate ALD is a practical necessity for the widespread adoption of ALD for many applications where film thicknesses in the 50-200 nm range are required. Superconducting quantum devices are one of these applications. These devices are comprised of superconducting resonators coupled to qubits. The operational frequency of the resonator is set by its geometry, but can be shifted undesirably by kinetic inductance effects, which depend on thickness. It is necessary to ensure that the superconducting resonator is thick enough to minimize the effect of kinetic inductance - typically by depositing 50-100 nm of material. Presently, these resonators are typically fabricated by sputtering, but sputtering has failed to meet other device needs, such as low loss at the superconductor-air interface and reproducibility of challenging nitrides. The challenge is to deliver fast processes while maintaining the desired film properties.

Here, we will share our recent development of high-quality superconducting NbN and TiN for quantum applications, such as resonators and interconnects, deposited at rates > 25 nm/hour, which is approximately 3x faster than previously reported. The RF-driven remote plasma source design and chamber of our ALD system are optimized to enable this high deposition rate.

The quality of the deposited films was demonstrated to be excellent, as measured by four-point probe electrical resistivity, conformality, and superconducting transition temperature (T_c). Good superconductive properties of the film were demonstrated by SQUID measurement. Thickness uniformity of < ±5% across a 150 mm Si wafer was achieved with good repeatability. We will also show how stress can be tuned as a function of process parameters.

Emerging quantum technologies based on superconducting nitride materials are showing great promise and will benefit not only from the uniformity of the deposition, conformality and film quality, but also from the speed and control provided by this ALD process.

2:45pm **AF1-TuA-6 Black TiO_2 Synthesized using Plasma-Enhanced Atomic Layer Deposition (PEALD)***, S. Berriel, **Terrick McNealy-James**, B. Butkus, T. Currie, C. Chen, L. Shultz, C. Feit, K. Davis, T. Jurca, P. Banerjee,* University of Central Florida

Black TiO_2 is a name given to TiO_2 in its heavily reduced state. This unique form of TiO_2 is characterized by its black color and optical absorbance from UV to infrared spectrum. Accordingly, black TiO_2 has been used as a light absorbing layer in solar cells, catalyst for H_2 generation and for the removal of environmental contamination. To date, black TiO_2 has been synthesized in various form factors such as single-phase nanoparticles using hydrogen thermal treatment, core-shell nanoparticles using high-pressure hydrogen treatment, and thin films using ambient hydrogen-nitrogen treatment of TiO_2 films. However, very little has been reported on ALD of black TiO_2 till date.

In this paper, we report on the synthesis of black TiO_2 using plasma enhanced atomic layer deposition (PEALD) deposited using alternate pulses of titanium tetraisopropoxide (TTIP) and Ar/H_2 plasma. The PEALD process was conducted at 200°C with a remote plasma and a TTIP temperature of 80°C. The films were characterized using *in situ* spectroscopic ellipsometry, four-point probe resistivity, UV-vis spectrometry, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Our data shows a higher growth rate for this PEALD process than for thermal ALD using TTIP, ~0.2 Å/cy and ~0.12 Å/cy respectively. Further, we find that black TiO_2 produced via PEALD is a conducting film. The utility of these films is assessed i) as carrier-selective contacts in Si solar cells and, ii) as photocatalysts for studying model dye degradation.

3:00pm **AF1-TuA-7 Optimizing for the Neutral Radicals in Plasma Enhanced ALD***, **Lauren Otto**,* Laminera

ALD has long been an enabler of cutting edge silicon technologies but is not without its issues. Ammonia used in thermal ALD of TiN causes leakage issues with DRAM capacitors. Thermal ALD films have higher impurities and high resistivities, and thermal ALD requires processing at high wafer temperatures (≥400ºC). PEALD was developed to reduce processing temperatures, but ions in PEALD are aggressive reactants and often damaging during film growth like in 3D NAND gate formation with ALD TiN and CVD/ALD W. Plasma damage from ions, electrons, and photons can be an issue in traditional capacitively coupled plasmas (CCPs) as well as inductively coupled plasmas (ICPs) and can cause unwanted local electric fields, charge traps, surface roughening, contamination, and further issues. Neutral radical species are “gentler” reactants than their ionic counterparts and can mitigate issues in traditional ALD and PEALD while maintaining lower temperature deposition. At Laminera, we have worked with a neutral radical source (Mantis Deposition MATS30) to mitigate issues from plasma damage and developed a novel ALD vacuum system designed specifically for working with the mean free path limited (as they are likely to recombine upon close approach) neutral radicals. This talk will cover the science behind working with and designing for the neutral radicals, designing and commissioning a vacuum system for ALD with neutral radicals, initial characterization of TiN deposited using the neutral radical source, and next steps for further technology development and improvement.

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.

[1]: A. Mackus et al, Chem. Mater. 31 (2019) 1142

[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.

1. S. De et al., Dalton Trans. 50, 1166 (2021)
2. D. T. Lee et al., Matter, 2, 404 (2020)
3. H. Barton et al., ACS Appl. Mater. Interfaces, 12, 14690 (2020)
4. J. Mondloch et al., J. Am. Chem. Soc. 135, 10294 (2013)
5. P. C. Lemaire et al., ACS Appl. Mater. Interfaces, 9, 22042 (2017)
6. S. De et al., Inorg. Chem. 59, 10129 (2020)
7. A. Fateeva et al., Angew. Chem. Int. Ed., 51, 7440 (2012)

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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References

[1] Y. K. Lee, C. Yoo, W. Kim, J. W. Jeon, and C. S. Hwang, “Atomic layer deposition of chalcogenides for next-generation phase change memory,” J. Mater. Chem. C, 2021, 9, 3708

[2] Z. Jiang et al., “Next-generation ultrahigh-density 3-D vertical resistive switching memory (VRSM)-Part II: desigg guidelines for device, array, and architecture,” IEEE Transactions on Electron Devices, 2019, 66, 12, 5147

[3] K. Ding et al., “Phase-change heterostructure enables ultralow noise and drift for memory operation,” Science, 2019, 366, 210-215

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.

1 K. Yasuda et al, Jpn. J. Appl. Phys. 22(10A), L615 (1983).

2 S.-W. Lee et al, in AVS 20th Int. Conf. At. Layer Depos. (Virtual, 2020).

3 A. Valdivia et al, J. Vac. Sci. Technol. Vac. Surf. Films 34(2), 021515 (2016).

4 J. Yang et al, ACS Appl. Mater. Interfaces 11(39), 36270–36277 (2019).

5 T.H. Baum et al, US11107675B2 (31 August 2021).

6 M. Juppo et al, J. Vac. Sci. Technol. A 16(5), 2845–2850 (1998)

ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-WeM

In Situ Measurement

Moderator: Prof. Mikko Ritala, University of Helsinki

8:00am **AF1-WeM-1 Measuring the Time-Resolved Heat of ALD Surface Reactions***, **Ashley Bielinski**, E. Kamphaus, L. Cheng, A. Martinson,* Argonne National Laboratory **INVITED**

Our understanding of ALD reactions is often limited to simplified and idealized models. Developing a mechanistic understanding of ALD surface reactions is beneficial in a wide range of applications such as optimizing film properties, interface engineering, and area- or site-selective ALD. *In situ* measurement techniques such as ellipsometry and IR spectroscopy are increasingly used to investigate ALD processes, but they primarily probe the ALD film between surface reaction steps. Pyroelectric calorimetry provides new insight into ALD processes by enabling quantitative and time-resolved measurement of the heat evolved in ALD surface reactions.

We report the total heat generation and heat generation rates for the ALD reactions between trimethylaluminum (TMA) and water to form Al_2O_3 as well as the ALD reactions between tetrakis(dimethylamino)zirconium (TDMAZr) and water to form ZrO_2 at different temperatures. The calorimetric data was combined with *in situ* spectroscopic ellipsometry and Rutherford backscattering spectrometry analysis of optical growth rates and composition. The total heat generation of each reaction was compared with the theoretical reaction enthalpy and first-principles computational models to investigate the reaction mechanisms and thermodynamics. While the calorimetric measurements of ALD reaction heat agree well with the calculated standard reaction enthalpies, there is significant spread in how the first-principles computational results compare to the experimental values. This enables evaluation of proposed models and mechanisms while providing a benchmark for future models. Additionally, the heat generation rate provides information on reaction kinetics. For example, the water reaction for ZrO_2 was found to proceed approximately 100× faster than the water reaction for Al_2O_3 and the TDMAZr heat generation rate suggests a kinetically resolved two-step reaction.

Pyroelectric calorimetry provides unprecedented measurements of ALD reaction heat with resolution down to 50ns and 0.1 $\mu J/cm^2$. This provides a unique opportunity to investigate how ALD surface reactions proceed to deepen our understanding of what drives and limits these processes.

8:30am **AF1-WeM-3 HfO_2 ALD on Si(111) - A Mechanistic in-Situ Study through Time-resolved APXPS***, **Rosemary Jones**,* Lund University, Sweden*; G. D'Acunto,* Stanford University*; P. Shayesteh,* Lund University, Sweden*; J. Gallet, F. Bournel, F. Rochet,* Sorbonne Universite, France*; I. Pinsard,* Lund University, Sweden*; A. Head,* Brookhaven National Laboratory*; J. Schnadt,* Lund University, Sweden

The introduction of atomic layer deposition, ALD, to the microelectronics industry has introduced a large number of new possible materials, able to be deposited in layers with atomic thickness control. One such material is the high-κ oxide HfO_2; thermally stable and ultrathin HfO_2 films deposited by ALD are a significant contender to replace SiO_2 as the gate oxide in capacitor applications. In such a device the typical support remains Si, and thus the HfO_2 gate oxide/Si interface is an integral part of the device. The characteristics of this interface can dramatically affect the overall performance of the device itself. We present a mechanistic study of the first deposition cycle of HfO_2 on the Si(111) surface using tetrakis(dimethylamido) hafnium (TDMA-Hf) and water as precursors using operando ambient pressure x-ray photoelectron spectroscopy (APXPS). This methodology allows us to observe the chemical reactions in a time-resolved manner, giving details of mechanism and kinetics of the reaction. It is found that even low levels of moisture contamination at the 1×10^{-7} mbar level can dramatically affect the substrate and therefore the initial ALD cycle. Here, we show that the hydroxylation of the clean Si(111) surface by residual water vapour, resulting in a 0.3 monolayer coverage of hydroxyls, leads to instantaneous full surface coverage of TDMA-Hf. The change in the atomic ratio of Hf to C/N found during the first deposition half-cycle, however, does not match the assumed immediate ligand loss through reaction with surface hydroxyls. One would expect an immediate loss of ligands, indicated by a Hf:N ratio of approx. 1:3 as TDMA-Hf deposits onto the surface. However, a Hf:N ratio of 1:4 is seen until 2 minutes after exposure. In addition, there is no evidence that any removed ligands remain on the surface, skewing the Hf:N ratio. The ligand exchange mechanism proceeds a lot slower than expected with a possible initial physisorption step – in the order of minutes rather than seconds. The slower reaction kinetics have many implications in terms of the quality of the interface when conditions are compared to industrial ALD reactors. Industrial reactors work on much faster timescales and at higher pressures than observed in this study which could result with intact precursor left physiosorbed to the substrate unreacted. In addition, the moisture contamination observed in this study would be unavoidable at more standard ALD reactor pressures, which implies that residual water needs to be an important consideration for the ALD performance and eventual interface quality.

8:45am **AF1-WeM-4 In Situ Reflection High Energy Electron Diffraction Investigations of Epitaxial Growth and Crystallization of Gallium Oxide Thin Films***, **Alexandra Howzen**, N. Strandwitz,* Lehigh University

The precursor decomposition temperature sets the maximum growth temperature of the "ALD window" which often limits the structural perfection and crystallinity of the resulting films. Intermittent annealing in between precursor chemical exposures during ALD film growth has been explored previously and shown to increase density and improve the electrical properties of ALD films[1]. However, without direct monitoring of one or more of the physical properties of the films, it can be difficult to determine the nuances of film transformation, such as crystallization temperature, crystallographic texture, surface roughening, and dependence on gas ambient.

In this work we utilize a home-built thermal ALD system with integrated reflection high energy electron diffraction (RHEED) for *in-situ* monitoring of both the deposition of direct epitaxial films and the transformation of amorphous ultrathin films during *in-situ* post-deposition annealing. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. Gallium oxide thin films were grown at several temperatures using trimethyl gallium/Ozone precursors and monitored with RHEED during deposition and post-deposition annealing. Films grown at low temperature were amorphous and films grown at higher temperatures resulted in epitaxial growth of β-Ga_2O_3 on sapphire. The initial phases of a direct epitaxial β-Ga_2O_3 film on sapphire revealed RHEED streaks that were coincident with spots in the zero order Laue zone of the sapphire substrate's diffraction pattern within as few as 5 ALD cycles. Conversely, the blurring-out of the sapphire substrate's diffraction pattern is seen in RHEED during the growth of an amorphous Ga_2O_3 film. *In-situ* RHEED is then used to monitor the structural evolution of the films during an immediate post-deposition, high temperature anneal. Our unique setup allows us to closely monitor the structural evolution of the direct epitaxial and thermally transformed films. It also allows us to determine the conditions in which the metastable polymorphs of Ga_2O_3 form in epitaxial systems. The integration of RHEED with ALD offers a slow-motion picture of traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

[1] J.F. Conley, Y. Ono, and D.J. Tweet, Appl. Phys. Lett. **84**, 1913 (2004).

9:00am **AF1-WeM-5 Surface and Film Stress during ALD of Al_2O_3 and ZnO: *In Situ* Measurements Using Wafer Curvature Techniques***, **Ryan B. Vanfleet**, E. Sorinto, A. Cavanagh, V. Bright, S. George,* University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The *in situ* measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress decreases with increasing deposition temperature. These *in situ* temperature-dependent Al_2O_3 ALD film stresses are in good agreement with *ex situ* film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These *in situ* measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress

from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional *in situ* measurements explored the surface and film stresses during zinc oxide (ZnO) ALD using diethyl zinc (DEZ) and H_2O as the reactants. ZnO ALD showed interesting stress evolution with an initial compressive stress that evolves to tensile stress, then returns to compressive stress (Figure 1). The initial compressive and tensile stress is attributed to the nucleation and coalescence of islands during ZnO film growth. The largest steady-state compressive film stress measured during ZnO ALD was -150 MPa. ZnO ALD shows opposite surface stress behavior compared with Al_2O_3 ALD. The H_2O exposure results in a compressive stress, while the DEZ exposure yields a tensile stress. The magnitude of surface stresses from the DEZ and H_2O surface reactions range between 0.2 N/m to 0.4 N/m and may depend on the dominant crystal orientation at the film surface.

[1]O.M.E. Ylivaara et al., *Thin Solids Films***552**, 124 (2014)

9:15am **AF1-WeM-6 Chemisorption Mechanisms of Aminosilane Precursors during ALD of SiO_2: *in situ* Characterization and ab initio Study**, ***Khabib Khumaini**, H. Son, H. Roh, O. Kim, R. Hidayat, H. Kim, W. Lee,* Sejong University, Republic of Korea

The ALD of SiO_2 thin films using aminosilane-type precursors, such as DIPAS ($SiH_3(N^iPr_2)$), BDEAS ($SiH_2(NEt_2)_2$), or TDMAS ($SiH(NMe_2)_3$), is being used in dielectric deposition and multiple patterning processes. The chemisorption of silicon precursors during the ALD of SiO_2 can be studied by density functional theory (DFT) calculation and in situ characterization techniques [1]. DFT studies assumed that dialkylamino ligands of silicon precursors combine with H atoms of surface hydroxyl groups to form amine molecules as the byproduct. However, there was a lack of reports considering the type and distance of the hydroxyl groups on the surface. In addition, in situ characterization for comparative studies of precursors with different numbers of dialkylamino ligands is also lacking. Therefore, in this study, we compared the chemisorption of aminosilane-type precursors on different OH-terminated SiO_2 surfaces modeled with different hydroxyl types and distances by DFT simulation. We also compared the chemisorption reactions of DIPAS and BDEAS, the precursors having different numbers of dialkylamino ligands. Reaction energies were calculated for all possible reaction pathways, and then the activation energies were obtained for exothermic pathways. Finally, we compared the number of released ligands (n) from the DFT simulation result with the experimental results from *in-situ* quartz crystal microbalance (QCM). For DIPAS, the DFT predicted that the chemisorbed species would be $–SiH_3^*$, which agrees with QCM and FTIR observation. DFT predicted that chemisorbed species of BDEAS would be $–SiH_2(NEt)^*$ and $–SiH_2^*$ depending on the type of hydroxyl group, which is consistent n ~ 1.5 ligands calculated from QCM. Therefore, the surface species predicted by DFT simulation well explains the experimental results from in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared (FTIR) spectroscopy.

9:30am **AF1-WeM-7 Seeing It Happen: Insights Into the Surface Chemistry of HfO_2 and TiO_2 ALD from *Operando* Ambient Pressure X-ray Photoelectron Spectroscopy**, ***Joachim Schnadt,*** Lund University, Sweden **INVITED**

The development of ALD processes is based on a number of different considerations and factors. One consideration is the envisaged ALD surface chemistry, which has to match not only the desired process outcome and processing conditions, but also the reaction properties of both the precursor and the surface. For many precursors, their surface chemistry is assumed to follow general reaction schemes. For example, the thermal ALD of transition metal oxides from amido complex and water precursors is typically assumed to follow a ligand exchange mechanism. The wide spread of such general reaction schemes results from that they often provide a sufficiently successful prediction of the ALD process outcome, but also because experimental tools are lacking that allow direct insight into reaction mechanisms. Indeed, it has been noted that surface chemistries can be both more complex and varied than general reaction schemes make believe [1,2].

Methods that allow the time-resolved monitoring of ALD processes, such as quartz crystal microbalance measurements, quadrupole mass spectrometry, pyroelectric calorimetry and ellipsometry provide deepened insight into ALD surface reaction mechanisms. More recently, these methods have been joined by two chemically sensitive techniques for the time-resolved characterisation of ALD processes, namely infrared spectroscopy [3] and ambient pressure x-ray photoelectron spectroscopy (APXPS) (cf., e.g., [4,5]). These two methods are capable of following the ALD surface chemistry in real time and at processing pressures equal or similar to those in an ALD reactor.

Using the metal amido complex- and water-based ALD of HfO_2 and TiO_2 on different surfaces as examples, I would like to demonstrate the usefulness of time-resolved APXPS for the elucidation of surface species and their evolution as well as for the observation of substrate processes such as oxygen transport. Such information allows to formulate ALD reaction mechanisms. In specific cases, we observe reaction pathways that deviate from the standard models of ALD surface chemistry, we find that surface hydroxylation is not always a prerequisite for oxide ALD, and for reducible supports we find that oxygen ion transport may play a major role in the initial ALD. Hence, APXPS provides us with entirely new information on ALD reaction mechanisms, which is important input for the future optimisation of ALD processes.

1. F. Zaera, Coord. Chem. Rev. **257**, 3177 (2013)
2. N. E. Richey et al., J. Chem. Phys. **152**, 1 (2020)
3. B. A. Sperling et al.,J. Vac. Sci. Technol. A **32**, 031513 (2014)
4. R. Timm et al., Nat. Commun. **9**, 1412 (2018)
5. G. D'Acunto et al., Chem. Mater. **35**, 529 (2023)

ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-WeM

High Aspects

Moderator: Prof. Riikka Puurunen, Aalto University, Finland

10:45am **AF2-WeM-12 Preparation and Characterization of Well-Defined Mixed-Oxide and Metal-Oxide Interfaces in Porous Catalysts using ALD**, ***Francisco Zaera,*** Department of Chemistry

As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites, with a particular focus on the design of unique mixed-oxide and metal-oxide interfaces for catalysis.

First, we will provide details on the deposition and characterization of alumina and titania films on SBA-15, a silica support with well-defined nm-sized one-dimensional pores, and for the growth of silica films on alumina supports. Specific issues related to ALD on porous solids will be highlighted, including possible incomplete deposition inside the pores and possible precursor condensation and pore clogging.

Characterization of the deposition process and the resulting oxide films will be presented, with emphasis on the use of pore size distributions, pore area and pore volumedata from N_2 adsorption-desorption isotherms to follow the rate and quality of the film growing process. The assessment of the initial nucleation steps using NMR will also be introduced, and a discussion on the crystallinity and optical properties of the resulting films will be provided. The quantitative determination of the evolution of the surface hydroxide sites that act as nucleation centers using infrared absorption spectroscopy (IR) will be illustrated.

The unique properties of the mixed-oxide surfaces produced via ALD will be discussed. These include the creation of new Lewis and Brønsted acid sites, which can be titrated by using IR, and the ability of the new surface sites to undergo facile and reversible reduction-oxidation interconversions, as seen by IR-based CO titrations as well as by EPR spectroscopy.

Finally, new catalysts were made by adding nanoparticles of metals such as gold or platinum into these ALD-made mixed-oxide solids, either before or after the ALD. The final products were tested for reactions such as CO oxidation and the selective hydrogenation of CO_2 and of unsaturated aldehydes. In all cases, optimum catalytic performance was observed at half a monolayer of the coverage of the new oxide, strongly suggesting that the active catalytic sites may be comprised of mixed oxide local structures involving Si–O–Ti or Si–O–Al bonds. It is thanks to the sub-monolayer control of the thickness of the deposited films that such optimum catalytic performances could be attained.

11:00am **AF2-WeM-13 A Toolbox for Characterization of Film Penetration Depth in High Aspect Ratio Structures***, **Anish Philip**, M. Utriainen, J. Kinnunen, P. Hyttinen,* Chipmetrics Ltd, Finland*; V. Korpelainen, B. Sauvet,* VTT Technical Research Centre of Finland*; W. Kessels, M. Poll, B. Macco,* Eindhoven University of Technology, The Netherlands

3D semiconductor devices have often dry etched vertical high aspect ratio holes, with 20 -200 nm critical dimensions. Conformality of the ALD/CVD thin film process in those high aspect ratio (HAR) structures is important for the functionality of the devices. HAR structures can be either lateral (LHAR) or vertical (VHAR). In this study, we focused on two less known factors of ALD growth in HAR structures, namely difference between vertical and lateral HAR geometries as well as the effect of the surface roughness. The PillarHall® lateral high aspect ratio (LHAR) test structure and measurement method is an effective way for fast and easy conformality characterization of the thin film processes[1]. PillarHall LHAR is a wide trench with nominal gap height 500 nm.The unique feature of PillarHall LHAR-method is an accurate and repeatable film penetration depth (PD) profile that allows to quantify step coverage for any aspect ratio as well as to characterize reaction kinetics in the sub-micrometre dimensions and molecular diffusion conditions. The compared HAR structures (Fig.1) were on commercial test chips VHAR1 (vertical holes) and PillarHall LHAR4 (lateral trenches) by Chipmetrics Ltd, as well as a modified version of LHAR chip (M-LHAR). The ALD process used in this study was TMA/H_2O Al_2O_3 at 300 °C in Beneq TFS-200. The Gordon model [2] is a useful approach to compare and predict the film PD performance in both HAR structure types. According to Gordon model, all structures had the same feature dimensions while their roughness varied. An inverse relationship between surface roughness and PD was revealed as the measured PD was highest for M-LHAR (Rq=0.17 nm) and lowest for VHAR1 (Rq=4.8 nm). The results indicate that surface roughness together with HAR geometry and gap height are the important factors that affects the model accuracy. In this study, NIR optical reflectometry was used to precisely measure the lateral trench gap height. We show also initial results from highly sensitive and PillarHall compatible measurement tools, such as contrast imaging SEM, UV-reflectometer (Fig.2) and imaging ellipsometer. They enable to measure PD of ultra-thin films with thickness < 10 nm. The presented toolkit concept is an efficient platform consisting of several well-specified test chips, measurement instruments, and modelling tools to execute highly accurate and repeatable film penetration depth analyses of ALD processes.

References

1. J. Yim and O. M. E. Ylivaara et al., Phys. Chem. Chem. Phys., 22 (2020), 23107
2. R. G. Gordon et al., Chem. Vap. Deposition, 9 (2003),73

11:15am **AF2-WeM-14 Understanding Process Parameters of ALD on Silica Aerogels and Their Effects on Mechanical Properties***, **Victor Vogt**, A. Gayle, Z. Berquist, A. Manon, A. Lenert, N. Dasgupta,* University of Michigan

Atomic layer deposition (ALD) is a powerful tool to modify ultra-high-aspect-ratio structures with unparalleled conformality. We have recently demonstrated the ability of ALD to modify silica aerogels with aspect ratios greater than 60,000:1 and improve their thermal stability from ~600°C to ~800°C, for applications in concentrated solar thermal energy generation.[1] To facilitate conformal ALD modifications on these extreme aspect ratios, a reaction-diffusion model was developed to precisely predict infiltration into the aerogel as a function of exposure time and number of doses, enabling tunable control of the infiltration depth.[2] To build upon this work, in this study, we examine the impact of key process parameters, including deposition temperature, precursor temperature, and purging procedures, and quantify the manufacturing tradeoffs between total ALD process time and precursor utilization. Additionally, we quantify the impacts of ALD modification on the optical, thermal, and mechanical properties of silica aerogels, which are critical for their usage in solar thermal applications.

In this study, we have built upon our previous reaction-diffusion model to explore the effects of deposition temperature, precursor temperature, and purging procedure on throughput and precursor utilization. A non-intuitive inverse relationship is observed between deposition temperature and infiltration depth, which is attributed to ideal-gas-law effects on precursor dosing, and this relationship is confirmed experimentally. Next, the impact of single cycle alumina-based modifications on mechanical properties is explored through 3-point bend and compression testing, including localized strain mapping via digital image correlation (DIC). The ALD modification is found to increase the elastic modulus of silica aerogels, and the results are compared with density scaling relationships for bare silica aerogels established in literature. Understanding the effect of ALD modification on aerogel mechanical properties is critical to implementation in engineering applications and provides a potential new pathway to tailoring the mechanical properties of aerogels and other high aspect-ratio structures.

References:

[1] Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **2022** *32*, 2108774.

[2] A.J. Gayle, Z.J. Berquist, Y. Chen, A.J. Hill, J.Y. Hoffman, A.R. Bielinski, A. Lenert, and N.P. Dasgupta, Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling, *Chem. Mater.* **2021** *33* (14), 5572-5583.

11:30am **AF2-WeM-15 Tuning Properties of ZnO Deposited via ALD for Applications in Sensing and Porous Material Development***, A. Coclite, **Lisanne Demelius**,* Graz University of Technology, Austria **INVITED**

The material properties and application related to zinc oxide, ZnO,have been heavily researched for decades and still produces new scientific output every year. ZnO is characterized by versatile and unique material properties that are an asset for applications ranging from cosmetics to optoelectronics. Emerging applications employ ZnO in transparent conductive oxides or piezoelectric nanogenerators. In particular, atomic layer deposition allows to deposit ZnO with a preferential orientation, which depends on the growth temperature and is directly liked to its piezoelectricity. In this talk, an example of application of piezoelectric ZnO deposited from ALD will be shown for sensing. A force, humidity and temperature responsive electronic skin will be presented, obtained by combining piezoelectric ZnO and a thermoresponsive hydrogel into core-shell nanostructures using ALD and initiated chemical vapor deposition.

In addition, introducing porosity to ZnO thin films increases the performance drastically and opens up new fields of applications. Different methods were used to deposit porous ZnO i.e., ALD growth in non-saturated conditions or by using organic spacers which were subsequently eliminated by calcination. In-situ ellipsometric porosimetry showed that films with porosity up to 24% were obtained. Metal-organic frameworks of ZIF-8 were synthesized by subjecting porous ZnO thin films to a 2-methylimidazole vapor. The impact of the porosity of the ZnO films onto the resulting ZIF-8 layers will be shown. Our results provide new insight into the link between deposition parameters of PE-ALD deposited ZnO and properties of the resulting ZIF-8 thin films – namely crystallographic orientation, thickness, coverage and roughness – thus making it possible to tailor them towards specific applications.

ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-WeA

Computational ALD I

Moderators: Prof. Dr. Michael Nolan, University College Cork, Atsushi Sakurai, ADEKA CORPORATION

1:30pm **AF1-WeA-1 Effect of Inhibitor Adsorption on the Mechanisms for Selectivity Loss*, Tania Sandoval,*** Technical University Federico Santa Maria, Chile **INVITED**

Area selective atomic layer deposition (AS-ALD) addresses some of the challenges that can occur in nanofabrication of complex multilayers structures, where different surfaces require patterning and alignment at the atomic scale. In this case, AS-ALD allows ALD to occur only on the surface that is desired through different strategies that include the use of inhibitor molecules. For the past few years, the use of small molecule inhibitors (SMIs) has gained attention as they show promise for implementation in high-volume manufacturing. However, selectivity values continue to be low, which could be attributed to the challenges in achieving suitable selective adsorption, and the need for understanding of the mechanisms behind selectivity loss.

In this presentation, theoretical studies on the fundamental understanding of the mechanism for selectivity loss will be discussed. Using a combination of both static and dynamic density functional theory (DFT) calculations, insights into t he displacement of acetylacetone by trimethylaluminum (TMA) and dimethylaluminum isopropoxide (DMAI) were studied. The results revealed the dependence between the inhibitor adsorption configuration, temperature, and selectivity loss. Due to the high reactivity and small size, TMA shows a higher probability to displace adsorbed Hacac than DMAI. We found that the adsorption mechanism for the SMI influence the probability of displacement, as the energetics determines the driving forces of the process. Moreover, by calculating thermochemistry it is possible to determine the extent of how much the selectivity can be improve with temperature within the AS-ALD process.

Overall, these results are keen in helping with proper selection of inhibitor molecules for AS-ALD.

2:00pm **AF1-WeA-3 Electronic Structure of ALD Al_2O_3/TiO_2 Heterointerfaces: A First-principles Study*, Hyobin Eom,*** *C. Ahn, J. Park, B. Shong,* Hongik University, Republic of Korea

Two-dimensional electron gas (2DEG) is a group of free electrons that is localized at thin region at an interface. 2DEG often exhibits high anisotropic carrier mobility along the in-plane horizontal direction, and large charge concentration. Because of such advantages, 2DEG can be applied to semiconductor devices such as high-electron-mobility transistors (HEMTs). Recent studies show that quasi-2DEG can be manifested at Al_2O_3/TiO_2 heterointerfaces formed via atomic layer deposition (ALD) [1]. Such low-lying donor states originate from the oxygen vacancy on the TiO_2 surface chemically formed by trimethylaluminum (TMA) [2]. In this work, various continuous bulk heterojunction structures of Al_2O_3 and TiO_2 with buried oxygen vacancies are studied through density functional theory (DFT) calculations. Analyses of density of states (DOS) along with local charge distribution show that the donor states are localized at the two-dimensional interface between Al_2O_3/TiO_2 where the oxygen vacancies are located. The structural stability of the heterojunction interface structures is confirmed using ab-initio molecular dynamics (AIMD) simulations. Non-equilibrium Green's function (NEGF) simulations prove high anisotropicity in electron transport of these structures. Current work provides atomistic understanding on electronic properties of ALD-formed emergent interfacial structures.

References [1] Chem. Mater. 2020, 32(18), 7662; [2] Mater. Today Adv. 2021, 12, 100195.

2:15pm **AF1-WeA-4 Reaction Mechanism of Bifunctional Organic Reactants and Diethylzinc for Atomic and Molecular Layer Deposition*, Miso Kim,*** *H. Oh, B. Shong,* Hongik University, Republic of Korea

In molecular layer deposition (MLD) processes, bifunctional organic reactants often show different growth behaviors depending on the chain length of their molecular backbone. For example, MLD using 1,2-ethanediol (1,2-ED) and diethylzinc (DEZ) results in organic-inorganic hybrid thin film of "zincone" containing stoichiometric amount of carbon.[1] In contrast, in a process using 1,5-pentanediol (1,5-PD) and DEZ, atomic layer deposition (ALD) of ZnO thin film without carbon impurities is reported.[2] Also, MLD thin films of Mo-thiolates shows decreased C content when dithiol with longer chain is used.[3] However, the molecular mechanism for the governing factor for removal of the carbonaceous moieties from the MLD thin films is yet unclear. In this study, the chemistry of DEZ and bifunctional organic reactants (linear $HX\text{-}C_nH_{2n}\text{-}XH$, X=O or S, n=2-6) according to the length of the backbone of bifunctional reactants was investigated through density functional theory (DFT) calculations. Several intramolecular reaction pathways in which $Zn\text{-}C_nH_{2n}\text{-}XH$ on the surface is converted to Zn-OH were investigated. By comparing the reactivity according to the backbone length of the bifunctional reactant structures, it was confirmed that the activation energy for forming Zn-XH decreases as the number of carbon increases, possibly resulting in inorganic ALD thin films without C.

References

[1] Chem. Mater. 2009, 21 (5), 820; [2] Chem. Mater. 2017, 29 (8), 3371; [3] J. Vac. Sci. Technol. A 2022, 40 (1), 012402.

2:30pm **AF1-WeA-5 Simulated Conformality of ALD Growth Inside Lateral HAR Channels: Comparison between a Diffusion-Reaction Model and a Ballistic Transport-Reaction Model***, J. Järvilehto, J. Velasco, J. Yim, C. Gonsalves,* ***Riikka Puurunen,*** Aalto University, Finland

Atomic layer deposition (ALD) is known for its ability to produce films of controllable thickness, even in narrow, high-aspect-ratio (HAR) structures [1]. These films can be highly conformal, meaning that the structure is covered by a film of uniform thickness [1,2]. However, when the structure's aspect ratio is increased sufficiently, deposition becomes limited by the diffusion of the reactants into the deep end of the structure, potentially resulting in the formation of an adsorption front, followed by a region of lower coverage [3]. Theoretical models have been developed to predict film conformality in HAR structures, as reviewed in Ref. 2.

This work presents a comparison of a diffusion-reaction model (DRM) developed by Ylilammi et al. [4,5] (Model A) and a ballistic transport-reaction model (BTRM) by Yanguas-Gil and Elam [6,7] (Model B). For the comparison, saturation profiles were generated using both models with similar simulation parameters (Knudsen number Kn >>1).

Qualitatively, both models produced similar trends in terms of half-coverage penetration depth and slope at half-coverage penetration depth. The saturation profiles were similar in shape, except for the film growth observed at the channel end in Model B. Quantitative examination yielded consistently higher half-coverage penetration depths in Model B. Model A produced steeper slopes at half-coverage penetration depth. In Model B, the discretization resolution was found to affect the penetration depth.

While the models gave qualitatively similar results, quantitatively extracted parameters differed. This finding is consistent with a previous comparison of a DRM and BTRM in the context of low pressure chemical vapor deposition [8]. The quantitative differences are relevant, for example, when the models are fitted to experimental data for the extraction of kinetic parameters, such as the sticking coefficient.

References

[1] J.R. van Ommen, A. Goulas, and R.L. Puurunen, "Atomic layer deposition," in Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 42 p. (2021).
[2] V. Cremers et al., Appl. Phys. Rev. 6 (2019) 021302.
[3] J. Yim and O.M.E. Ylivaara et al., Phys. Chem. Chem. Phys. 22 (2020) 23107-23120.
[4] M. Ylilammi et al., J. Appl. Phys. 123 (2018) 205301.
[5] J. Yim and E. Verkama et al., Phys. Chem. Chem. Phys. 24 (2022) 8645.
[6] A. Yanguas-Gil and J.W. Elam, Theor. Chem. Acc. 133 (2014) 1465.
[7] A. Yanguas-Gil and J.W. Elam, (2013) https://github.com/aldsim/machball, accessed Feb 13 2023.
[8] M.K. Jain et al., J. Electrochem. Soc. 140 (1993) 242.

2:45pm **AF1-WeA-6 Simulated Conformality of ALD in Lateral High Aspect Ratio Channels: Impact of Knudsen Number on the Saturation Profile*, Christine Gonsalves,*** *J. A. Velasco, J. Järvilehto, J. Yim, V. Vuorinen, R. L. Puurunen,* Aalto University, Finland

Due to its unparalleled conformality, atomic layer deposition (ALD) is often the method of choice for coating nanostructures having complex geometries with atomic level precision [1]. However, conformality in high-aspect-ratio (HAR) surface features evolves with time and depends on process parameters and chemistry [2,3]. Different models have been

developed to simulate ALD growth in HAR structures [2,3]: diffusion–reaction models, Monte Carlo models and ballistic transport–reaction models.

Studies of ALD growth in HAR (AR ≥ 100) features typically assume free molecular flow conditions (Knudsen number $Kn >> 1$), with the molecule's mean free path much larger than the feature size. However, depending on the limiting feature size and pressure, the free molecular flow assumption may not be fully valid in real ALD processes.

In this work, we mapped the evolution of conformality in lateral high-aspect-ratio (LHAR) channels in terms of the Knudsen number from free molecular flow governed by Knudsen diffusion ($Kn>>1$) through the transition regime (Kn~1) to continuum flow conditions governed by molecular diffusion ($Kn<<1$). The mapping was done by varying the LHAR channel height and reactant partial pressure; Knudsen number was varied by 13 orders of magnitude. Thiele modulus was kept above one, so that diffusion-limited conditions prevailed and the simplified model by Ylilammi et al. [4] re-implemented earlier [3], could be used for the simulations. Reactant exposure was kept constant.

When $Kn>>1$, regardless of the partial pressure of the reactant and the channel height, the same characteristic saturation profile was obtained. When Kn~1 and $Kn<<1$, the penetration depth decreased and the steepness of the adsorption front increased with decreasing Knudsen number.

The slope method by Arts et al. [5] was used to back-extract the sticking coefficient from simulated saturation profile, up to demonstrating how the slope method breaks when conditions deviate from free molecular flow. Using the slope method for conditions where the Knudsen diffusion assumption is not valid, would lead to an incorrect (too high) interpretation of the sticking coefficient (even unphysical values above one).

References

[1] J.R. van Ommen et al., "Atomic layer deposition," in Kirk Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc. (2021).

[2] V. Cremers et al., Appl. Phys. Rev. 6 (2019) 021302.

[3] J. Yim, E. Verkama et al., Phys. Chem. Chem. Phys. 24 (2022) 8645.

[4] M. Ylilammi et al., J. Appl. Phys. 123 (2018) 205301.

[5] K. Arts et al., J. Vac. Sci. Technol. A. 37 (2019) 030908.

3:00pm **AF1-WeA-7 Atomistic Modeling of Thin-Film Deposition with Carrier Gases**, *S. Natarajan, P. Khomyakov, J. Wellendorff,* Synopsys Denmark*; **Baiyu Zhang**, A. Blom,* Synopsys, Inc.

Advances in thin film deposition techniques are at the core of atomically fine-tuned manufacturing of next-generation semi-conductor devices. Extreme fabrication limits require optimization of existing and development of new thin film deposition setups for maximum process capability and yield. In silico modeling approaches can be of particular importance when developing new deposition processes where experimental data are unavailable or expensive and time-consuming to obtain. We have previously shown how machine learning based atomic-scale modeling of ALD processes, e.g., ALD of HfO_2, [1] with Synopsys QuantumATK software [2,3] was used to simulate energetics, dynamics, and mechanisms of precursor molecule interaction with a substrate material, and provide important parameters, such as sticking probabilities and growth rates, for further physical modeling with topography tools, such as Sentaurus Topography.

In this talk, we will present an enhancement of this deposition simulation workflow by including the effect of carrier gases. The impact of carrier gases becomes critical at higher pressures, as carrier gas molecules collide with precursor molecules and alter growth rates. We will demonstrate the enhanced complete workflow in QuantumATK, including density functional theory-based thermochemistry, reaction kinetics and classical molecular dynamics, and show results for Si deposition using disilane precursor and hydrogen carrier gas at varying pressures.

In the first step, we identify the most probable reactive gas phase species and evaluate their equilibrium concentrations in gas mixtures, which are present in the reactor at the process conditions. This is achieved by comparing Gibbs free energy profiles of many possible gas phase decomposition reactions. Since the above results do not include kinetic information, they are usually valid only when the activation barriers of the considered reactions are fully breached by thermal energy. Thus, in the second step, we compute reaction kinetics which involves obtaining rates and branching ratios of the most probable reactions from step 1 to identify the flux ratios of the reactive species. These flux ratios inform us of the fractions of the dissociated species in the reactor along with the intact precursor molecules at the process conditions. In the final step, we perform molecular dynamics simulations with the flux ratio from kinetic studies to compute the sticking probabilities and growth rates.

[1] J. Schneider et al., ALD 2022.
[2] S. Smidstrup et al. , J. Phys.: Conden. Matter 32, 015901 (2019).
[3] QuantumATK version V-2023.09, Synopsys QuantumATK.
(https://www.synopsys.com/silicon/quantumatk.html)

3:15pm **AF1-WeA-8 Chemistry of Plasma-Enhanced and Thermal Atomic Layer Deposition of Metal and Intermetallic Thin Films: The Role of Substrates and Reducing Agent***, **Ji Liu**, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Atomic layer deposition (ALD) is widely used in microelectronics and catalysis to deposit metal thin films. The key advantages of ALD are the conformality and precise thickness control at the atomic scale. Cobalt (Co) is an interesting material in the semiconductor industry due to its attractive electrical and physical properties. The replacement of Cu with Co as contacts or interconnects in semiconductor devices serves as an illustrative example and is an ongoing process driven by large device manufacturers.

In this presentation, I will present our recent work on the plasma enhanced (PE) and thermal ALD growth of Co from first principles calculations. For PE-ALD of Co using $CoCp_2$ and N-plasma, we first addressed the surface reaction mechanism in the metal precursor pulse and plasma half-cycle on NH_x-terminated Co surfaces, which corresponds to the steady growth for the PE-ALD. The reactions at the initial stages on a series of Si surface terminations are investigated to gain detailed atomic insights on the effect of different substrates on the elimination of Cp ligands.

For thermal ALD of Co, our collaborators have shown that Co thin films deposited with ALD are metallic and Zn-free. We modelled the reaction mechanism of $CoCl_2$(TMEDA) and a reducing agent, $Zn(DMP)_2$. Our DFT calculations indicate that the reactions proceed via initial ligand exchange of DMP and Cl on Co(111) surface with $CoCl_2$ termination and Zn is removed via ZnCl(DMP) formation and desorption, resulting $Co(DMP)_2$ termination on the surface. The two DMP ligands are removed via C-C bond formation in a straightforward way.

Further, we presented our recent collaborative work of a new type of ALD process for intermetallic FeZn thin films, where diethyl zinc (DEZ) serves as a coreactant. The $FeCl_3$ + DEZ process yields in situ crystalline Fe_4Zn_9 thin films. DFT calculations indicate that the favorable pathway of eliminating the Cl group and the Et ligand is via butane and subsequent EtCl formation and desorption.

Our DFT studies show that substrate terminations and reducing agents have significant impact on ALD deposited metallic thin films.

ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-WeA
Computational ALD II

Moderator: Dr. Tania Sandoval, Technical University Federico Santa Maria

4:00pm **AF2-WeA-11 Revealing Process-Structure Relationships for ALD Amorphous Oxide Semiconductors with XANES and First-Principles Modeling***, **Orlando Trejo**,* Applied Materials*; T. Cho,* University of Michigan, Ann Arbor*; S. Sainio,* University of Oulu, Finland*; N. Dasgupta,* University of Michigan, Ann Arbor

Amorphous oxide semiconductors (AOS) lack the long-range order characteristic of crystalline materials but possess short-range order that gives rise to a vast parameter space to design and optimize their properties. To accelerate efforts to control their functional properties and optimize device performance, an increased fundamental understanding of the complex process−structure−property relationships of AOS is needed. Recent research efforts have provided an initial framework to understand how short-range order in AOS determine their properties. The structure and interconnection of the metal-oxygen (M-O) polyhedra in AOS depend on the material system (i.e., the composition and types of elements) and the synthesis conditions (e.g., solution, physical or chemical vapor deposition). Given its atomic-level synthesis control and technological relevance, ALD chemistry facilitates and encourages a systematic structural analysis of AOS that are material and process specific.

In our previous work, we optimized the performance of amorphous ALD zinc tin oxide (ZTO) thin-film transistors by turning the Zn-to-Sn ratio and annealing temperature.[1] However, prior work has not been able to fully

uncover the mechanistic origins of the differences in performance among samples. To address this knowledge gap, here we leverage ALD's capability to finely tune the composition of ZTO films along with systematic annealing to reveal how cation composition and annealing temperature influence the geometric and electronic structure in an AOS.[2] The ZTO films are characterized with XRD, XPS, and synchrotron x-ray absorption near-edge spectroscopy (XANES) measurements of the O K-edge, Sn M-edge, and Zn L-edge. The XANES spectra are analyzed with ab initio and nonlinear statistical modeling. The resulting multimodal analysis of ALD ZTO reveals how process conditions give rise to gradual or abrupt changes in the coordination environment of the Zn−O and Sn−O polyhedra, which in turn translate into changes in the relative contribution of the Zn and Sn s orbitals to the density of states near the conduction band minimum. Thus, this multimodal X-ray analysis and modeling framework can be applied to understand the process-structure relationships needed to optimize AOS performance in devices.

(1) Allemang, C. R.; Cho, T. H.; Trejo, O.; Ravan, S.; Rodríguez, R. E.; Dasgupta, N. P.; Peterson, R. L., *Adv. Elec. Mater.* **2020**, *6*, 2000195.

(2) Trejo, O.; Cho, T. H.; Sainio, S.; Dasgupta, N. P., *J. Phys. Chem. C* **2023**, *127*, 338

4:15pm **AF2-WeA-12 Machine-Learning Aided Understanding of ALD Processes***, A. Arunachalam,* University of Texas at Dallas*; **S. Novia Berriel**, U. Kumar,* University of Central Florida*; S. Das,* University of Texas at Dallas*; S. Seal,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee,* University of Central Florida

ALD processes are controlled via an array of hardware-based, independent process parameters. Typically, 'recipes' are built that enable these parameters to be set to specific values during an ALD process. Example parameters include chuck and chamber temperatures, line and precursor temperatures, gas flow rates, etc. While each of these play an important role in the growth rate and final thickness of an ALD film, there is currently no measure of the magnitude of their impact on the film thickness and quality. Further, there is no way to predict film thickness purely based on process parameters without running numerous experiments to get an estimated growth rate. We propose the use of machine learning (ML) approaches to generate 'feature importance maps' that graphically depict the impact of these parameters in determining and predicting film thickness.

Our ML method begins with a set of 78 process parameters recorded from an ALD process from a Veeco® Fiji Gen2 ALD system for a CeO_2 film. The ALD process has been described in detail elsewhere[1]. A random forest ML algorithm then identifies the top-ten 'critical' independent process parameters that affect film thickness at a given deposition temperature. These include a list of heater zones around the reaction chamber, line pressure of the precursor delivery line, etc. A temperature dependent (from 185 °C – 320 °C) series is then generated. The model is able to predict with up to 99.99% accuracy the time variation of thickness during the growth, verified via in situ spectroscopic ellipsometry. Our talk will include detailed considerations in generating the ML model, as well as results for a range of process temperatures for CeO_2 ALD.

[1] U. Kumar, C. Feit, S. N. Berriel, A. Arunachalam, T. S. Sakthivel, K. Basu, P. Banerjee and S. Seal, Journal of Vacuum Science & Technology A 39, 060405 (2021).

4:30pm **AF2-WeA-13 Digital Twin and Experimental Platform for AI-Driven Optimization of ALD Processes***, **Angel Yanguas-Gil**, N. Paulson, J. Elam,* Argonne National Laboratory

Atomic layer deposition is an ideal platform for exploring AI-driven optimization and discovery: first, ALD's step-by-step nature defines a natural design space where a growth is defined by sequences of cycles, each of which driven by their own timings; Second, ALD tools already come with the required control software and hardware to integrate with AI engines. Finally, its integration into cluster tools with automatic wafer handling systems in microelectronics opens up the possibility of fully automatic growth-characterization-decision cycles to develop novel materials.

In this work we describe an experimental setup for AI-driven process optimization as well as a digital twin for the development and validation of novel algorithms for self-driving labs. Building on prior research where we used simulated quartz crystal microbalance data, here we expand the range of techniques to incorporate optimization based on in-situ spectroscopic ellipsometry. In addition to algorithms to optimize the dose and purge times of single processes, we have also explored algorithms to find optimal sequences of ALD cycles for binary and ternary compounds based on target optical properties.

From an experimental perspective, we have demonstrated the optimization of ALD processes based on in-situ techniques. While the results are demonstrated in a specific cross-flow reactor, the methodology and algorithms developed can be easily adapted to other reactor configurations and characterization techniques.

This research has been supported through Argonne's Laboratory Directed Research and Development program.

[1] Noah H. Paulson, Angel Yanguas-Gil, Osama Y. Abuomar, and Jeffrey W. Elam, ACS Applied Materials & Interfaces 2021 13 (14), 17022-17033. DOI: 10.1021/acsami.1c00649

[2] Angel Yanguas-Gil and Jeffrey W. Elam, Machine learning and atomic layer deposition: Predicting saturation times from reactor growth profiles using artificial neural networks, Journal of Vacuum Science & Technology A 40, 062408 (2022) https://doi.org/10.1116/6.0001973

4:45pm **AF2-WeA-14 Closing Remarks in Grand Ballroom H-K***,*

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