ALD Fundamentals
Room Halla Hall AB - Session AF1-MoA

ALD on 3D Structures

Moderators: Hao Van Bui, Phenikaa University, **Arrelaine Dameron**, Forge Nano

4:00pm **AF1-MoA-11 Continuous Production of Nanocoated Powders**, ***Sébastien Moitzheim,*** Powall, Netherlands **INVITED**

Powder-based processes are critical to a wide range of industries, from battery materials to pharmaceuticals. Achieving the desired performance often depends on precise surface modifications.Over the past decade, Powall has been developing a scalable nanocoating technology that combines the atomic-level precision of Atomic Layer Deposition (ALD) with the speed and throughput of Chemical Vapor Deposition (CVD), enabling continuous and cost-effective production.

In this presentation, Dr. Moitzheim (CTO) will share Powall's key learnings on transitioning gas-phase coating methods from lab to pilot-scale and beyond. Specific attention will be paid to how the technology can be adapted to accommodate powders of varying sizes, shapes, and porosities, while still ensuring uniform and high-quality coatings. The talk will also provide an update on the upcoming commercial pilot-scale equipment and outline the path toward large-scale manufacturing. By illustrating the core challenges and advancements in scaling powder nanocoatings, this talk will offer a balanced perspective for researchandindustry.

4:30pm **AF1-MoA-13 Plasma-Enhanced Spatial ALD on 2D and 3D Surface Topologies: The Case of Amorphous and Crystalline TiO_2**, ***Mike van de Poll,*** Eindhoven University of Technology, Netherlands; *Jie Shen,* Holst Centre / TNO, Netherlands; *James Hilfiker,* J.A. Woollam Co., Inc.; *Marcel Verheijen, Paul Poodt,* Eindhoven University of Technology, Netherlands; *Fieke van den Bruele,* Holst Centre / TNO, Netherlands; *Erwin Kessels, Bart Macco,* Eindhoven University of Technology, Netherlands

As of late there were two key research questions regarding the conformality of plasma-enhanced spatial ALD (PE-s-ALD): can the technique be used to deposit highly conformal films, and how do the material properties – like crystallinity and composition – of such films change throughout the coated 3D structures? We have recently answered the first question by showing that exceptionally conformal films can be grown by PE-s-ALD with subsecond plasma exposures, thanks to the high radical density in the atmospheric plasma [1]. However, various crystallization and growth effects can influence the film profile and crystallinity, and understanding these effects and their interplay is key.

In this work, we demonstrate the complex growth mechanism of TiO_2 using PE-s-ALD, and study conformality not just in terms of films thickness, but also in terms of film properties. TiO_2 films are deposited both on planar substrates and inside lateral high-aspect-ratio (LHAR) test chips (PillarHall^{TM} by Chipmetrics Ltd). These LHAR structures uniquely allow for spatial material property mapping in trenches using spectroscopic ellipsometry, Raman spectroscopy and X-ray photoelectron spectroscopy. Conditions that result in the anatase phase on a planar surface only partially form this phase inside LHAR structures, with the deepest part of the film being amorphous. This partial crystallization is ascribed to the film thickness inside the LHAR structure gradually dropping below the critical thickness for crystallization. In turn, the partial crystallization is shown to have a significant effect on the resulting thickness profile, due to an enhanced growth per cycle on crystalline surfaces. A framework of the interplay between effects is proposed, offering insights that enable better control of the crystallinity and thickness throughout the entirety of coated surfaces of 3D structures by PE-s-ALD.

Additionally, the recombination probability of O-radicals during this atmospheric-pressure PE-s-ALD process at 200 °C is determined to be 3×10^{-5}, which is similar to low-pressure PE-ALD [2]. This result indicates that differences in conformality between the two types of ALD are not the result of differences in recombination probability, but rather of differences in initial radical density and diffusion behavior.

[1] van de Poll, M. L., Jain, H., Hilfiker, J. N., Utriainen, M., Poodt, P., Kessels, W. M. M., & Macco, B. (2023). *Applied Physics Letters*, *123*(18), 182902.

[2] Arts, K., Deijkers, S., Puurunen, R. L., Kessels, W. M. M., & Knoops, H. C. M. (2021). *Journal of Physical Chemistry C*, *125*(15), 8244–8252.

4:45pm **AF1-MoA-14 Rapid Test for ALD in High Aspect Ratio Spaces Utilizing Thermally Bonded Chips and Hydrazine with Titanium Tetrachloride for TiN Deposition**, *Amy Ross, Dipayan Pal, Dohyun Go, Diego Contreras Mora, Ping-Che Lee,* UC San Diego; *Danish Baig,* Georgia Institute of Technology; ***Adrian Alvarez,*** RASIRC, USA; *Dan Le, Jeffery Spiegelman,* RASIRC; *Muhannad Bakir,* Georgia Institute of Technology; *Andrew Kummel,* UC San Diego

The increasing demand for high-bandwidth memory necessitates the development of devices with 3D structures, such as DRAM. These devices rely on the deposition of conformal, particle-free films with complete coverage in high-aspect-ratio (HAR) spaces. Transmission electron microscopy (TEM) is the standard technique for verifying these parameters, but it is costly, time-intensive, and only inspects a very small area of the surface of interest. This study demonstrates a rapid and non-destructive alternative involving thermally bonded chips that provide HAR spaces for deposition. The chips can be debonded and analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM).ALD titanium nitride (TiN), typically utilized as a 2 nm diffusion barrier between tungsten (or copper) and SiO_2 (or SiCOH) in HAR spaces, was employed using $TiCl_4$ and N_2H_4 precursors, to deposit a 20 nm layer in a thermally bonded chip with a 2000:1 aspect ratio (fig. 1). This is 10x the normal thickness of diffusion barriers to increase sensitivity to particle formation.

A control test was conducted on a clean, thermally bonded sample with no TiN deposition (fig 2). The debonded dies were analyzed as planar samples using AFM, SEM, and energy-dispersive spectroscopy (EDS), confirming no detectable titanium (0% atomic percent) in any region (edge, middle, center). The AFM RMS was measured at 2.06 nm. For TiN deposition, increasing precursor doses 1×, 2×, and 3× normal exposure (1x = 500 ms $TiCl_4$, 2750 ms N_2H_4, 30 sec purge, substrate temperature 475°C) were employed to evaluate penetration depth and particle formation. The RMS roughness values for the top die remained low at 1.92 nm, 1.77 nm, and 1.64 nm, respectively. This indicates no particle formation. Atomic Ti percentages from EDS decreased as the effective aspect ratio increased from 475:1 to 2000:1 aligning with predictions from the Gordon Model [1]. Additionally, the 3x smaller %Ti decreases at the center between the 3× and 2× dose sample further support the model's estimation of precursor penetration. Temperature variations across the sample may have prevented complete surface saturation. The low RMS roughness and absence of large features suggest that CVD particle formation did not occur in the HAR space, consistent with the $TiCl_4$ + N_2H_4 chemistry avoiding $NH_4Cl(s)$ formation [2].

AFM was used to analyze an area of over 111 μm^2, revealing no defects or CVD particles. In comparison, a typical TEM survey covers only 0.004 μm^2. This means SEM/AFM in debonded chiplets examined a region ~30,000x larger than TEM allowing large area determination of particles formation in HAR.

5:00pm **AF1-MoA-15 Enhancing Step Coverage in High-Temperature Ald for Advanced Semiconductor Scaling**, *Seung Hyun Lee, Deok Hyun Lee,* Soulbrain Co., Ltd., Republic of Korea; *Kok Chew Tan,* Soulbrain Co., Ltd., Malaysia; *Sung Gi Kim,* ***Gyun Sang Lee****, Jung Hun Lim, Jae Sun Jung,* Soulbrain Co., Ltd., Republic of Korea

As semiconductor technology advances, improvements in performance, power efficiency, and area optimization continue to drive innovation. However, increasing device complexity and higher integration levels have exacerbated step coverage challenges during the deposition of high-k thin films in DRAM capacitors, metal gate insulators, and block oxides in 3D NAND. In particular, achieving uniform thin-film deposition on high-aspect-ratio patterns has become increasingly difficult. Additionally, the application of high-temperature processes to enhance film quality can lead to precursor decomposition, further deteriorating step coverage. To address this issue, this study proposes the use of inhibitor technology as an effective approach to improving step coverage in high-temperature atomic layer deposition (ALD) processes. Our experimental results demonstrate that the inhibitor remains stably adsorbed on the substrate surface under various ALD conditions, effectively mitigating step coverage issues. Notably, this inhibition effect persists even at temperatures above 600°C during the growth of Al_2O_3 thin films. Furthermore, a newly developed hydrocarbon-based inhibitor has been identified as optimal, as it fully decomposes into water and carbon dioxide upon reacting with ALD precursors, leaving no residual impurities in the film.

5:15pm **AF1-MoA-16 ALD as the Solution for Uniform Cu Electroplating in High Aspect Ratio Vias***, **Matthew Weimer**, Sara Harris,* Forge Nano*; Irina Stateikina,* Centre de Collaboration MiQro Innovation (C2MI), Canada*; Dane Lindblad,* Forge Nano*; Marc Guilmain, Xavier Gaudreau-Miron,* Centre de Collaboration MiQro Innovation (C2MI), Canada*; Arrelaine Dameron,* Forge Nano

Scaling interconnects to increase device density is a critical bottleneck for a range of applications in the 3D and advanced packaging field. Currently, interconnect density is limited by, amongst other things, the ability to produce reliable, low resistivity, Cu vias at high aspect ratios (AR). Some microelectromechanical system (MEMS) applications, where the interconnect in the device layer is defined by the size of the active component, called the proof mass, are restricted in height due to fabrication limitations of high AR interconnects. As a result, some device architectures are inaccessible, limiting the utility of devices, such as high-sensitivity inertial sensors. While some progress has been made, single-side deposition used in blind vias is limited to 8:1 or less. The source of that limitation is the physical vapor deposition (PVD) processes used to apply adhesion and/or nucleation layers required for successful Cu electrochemical deposition (ECD). PVD provides high-quality layers, but those layers are applied in a non-conformal fashion, leading to device failure in non-line-of-site or high AR features, as shown in Figure 1. We have been working on a complete thermal ALD solution at <300 °C consisting of a high-quality SiO$_2$ dielectric barrier, breakdown voltage >12 MV/cm, a dense TiN Cu diffusion barrier, density ~5.0 g/cm^3, which also functions as a Ru nucleation layer, and low resistivity Ru metal Cu seed layer, resistivity <20 $\mu\Omega\cdot$cm at 20 nm. In this work, we demonstrate successful Cu seed application by depositing this ALD dielectric/diffusion barrier/Cu seed layer stack on Si trenches, where the state-of-the-art PVD solution has multiple failure modes. Successful conformal ECD has been demonstrated with 15-20 nm of Ru in vias with AR from 4:1 to 25:1 and in through glass vias (TGV) with AR from 6:1 to 30:1. Further tests are ongoing with collaborators at the National Institute of Standards and Technology (NIST) to refine Cu ECD conditions and measure via resistivity of Cu ECD in the vias.

5:30pm **AF1-MoA-17 Multi-Scale Model for Optimization of Low-Temperature Al$_2$O$_3$ ALD Process Conformality Within High Aspect Ratio Trench***, **Ivan Petraš**, Yury Shustrov, Andrey Smirnov,* Semiconductor Technology Research d.o.o. Beograd, Serbia

ALD is typically characterized by two main steps with self-limiting reactions on the surface and purging. Each step requires a certain time to ensure complete coverage of the surface by precursor and complete removal of the precursor from the reactor volume during the purging steps. ALD process optimization requires achieving the minimal ALD cycle duration while preserving good conformality within the trench structures over the wafer surface. Optimal process conditions are changed with respect of the trenches pattern, trench surface density and aspect ratio. Therefore, the process adjustment on the blanket wafers becomes inefficient, while the adjustment cost with the patterned wafers is typically high. In this sense, multi-scale models with the coupled reactor-scale and feature-scale simulations can be applied for reducing of process development costs. Focus of this work is aimed at the improvement of low-temperature Al2O3 ALD performance with consideration of patterned wafers through adjustment steps duration and operating conditions. An integrated modeling approach was developed with self-consistent coupling of modeling tasks on different scales. The reactor-scale model of TMA delivery, oxidation by H2O and purging includes unsteady mass transport with surface chemical reactions. The trench-scale model includes tracing TMA and H2O species as well as products of surface chemical reactions.It is demonstrated that increasing of trench aspect ratio leads to remarkably longer time for achieving of ALD conformality on patterned wafer during both TMA delivery and oxidation steps. The increase of precursor impulse duration results in the reducing of time required for full coverage, but simultaneously it increases the needed time for purge step before introduction of the next precursor. As the result the increasing the precursor pulse duration for better conformality within the trench may lead to requirements of longer time for ALD cycle and thus decrease the throughput of the process. Pressure effect on the trench coverage time demonstrates different trends with the aspect ratio change during TMA and H2O steps. At lower aspect ratio of 20 the pressure decrease leads to faster trench coverage, while for high aspect ratio of about 100 there is the non-monotonic behaviour of coverage speed with pressure change. It is demonstrated that a detailed consideration of low temperature oxidation mechanism is important to correctly describe the oxygen incorporation into the film and resulting ALD conformality. Effect of temperature and H2O purge step duration on the resulting film stoichiometry are discussed.

ALD Fundamentals
Room Tamna Hall B - Session AF2-MoA

Precursor Chemistry I

Moderators: Seán Barry, Carleton University, **Haripin Chandra**, EMD Electronics, USA

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

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

4:30pm **AF2-MoA-13 Perspective on Beryllium Compounds as Precursors for ALD Applications***, **Dominik Naglav-Hansen**,* Ruhr University Bochum, Germany*; Magnus Buchner,* University of Marburg, Germany*; Martin Wilken,* Ruhr University Bochum, Germany*; Deniz F. Bekiş,* University of Marburg, Germany

Until this day there has been almost no development of beryllium precursors with tailor-made properties for their application in ALD processes, be it the deposition of Be-metal, BeO or Be$_2$N$_3$-layers on any kind of substrate. Since these three beryllium based materials are of high importance in the microelectronics industry and for high performance ceramic materials, it is somehow confusing that not much research been done in this field so far. [1-6] One reason might be the „infamous“ toxicity of beryllium and its compounds, which hindered progress in the field of beryllium chemistry for ages. The authors of this work contributed a lot to this debate in the past. [7-13] However, the development of volatile beryllium compounds is still scarce and to the best of our knowledge no systematic studies and experiments were performed until today. In this perspective work the concepts and preliminary results of several beryllium compounds, which differ in their chemical compositions, bonding modes and physico-chemical properties, are presented and discussed. First insights into the relationship between the chemical and electronic structure of those compounds and their influence on their volatility are highlighted. Proof of concept depositions for different classes of beryllium based thin films are planned to be presented opening the gate to a new way of making these materials.

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

Metal halides are an emerging group of compounds with a steadily increasing number of ALD processes published each year.[1] Most metal halide ALD processes employ volatile metal halides, such as TiX$_4$ or SnX$_4$, as halide (X = F, Cl, Br, I) precursors. ALD processes were first developed for metal fluorides using HF, with a later transition towards volatile metal fluorides (for example, TiF$_4$ and TaF$_5$) as safer and less corrosive alternatives to HF. The main applications of metal fluoride films are in optics and batteries.

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

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

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

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

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

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

5:00pm AF2-MoA-15 Evaluating Trisilylamine and Diiodosilane as Silicon Precursors for PEALD of Silicon Nitride in Front-End-of-Line Applications,

Keerthi Dorai Swamy Reddy, *Marco Lisker,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany

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

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

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

5:15pm AF2-MoA-16 Precursor Design for Thermal ALD of Silver Metal,

David Emslie, *Nick Hoffman,* McMaster University, Canada

Thin films of metallic silver are of interest as transparent electrodes for solar cells and LEDs,[1] and in photonics/plasmonics.[2] ALD is a uniquely capable method for the deposition of highly uniform and conformal thin films, and a handful of methods for silver thermal ALD have previously been reported. For example, several publications describe the use of [(hfac)Ag(COD)] (hfac = hexafluoroacetylacetonate; COD = 1,5-cyclooctadiene) as a precursor for Ag ALD, in combination with ^{n}PrOH[3-5] or ^{t}BuNHNH$_2$[4] as the co-reactant. However, the [(hfac)Ag(COD)] precursor is thermally unstable and requires direct liquid injection, and the reported processes exhibit a narrow (5–23 °C) temperature window. ALD methods have also been reported using [(hfac)Ag(PMe$_3$)] (Me = methyl) in combination with formalin ($H_2C{=}O/H_2O$),[6] or in a multi-step process involving reactions with $AlMe_3$ and then H_2O.[6] However, these methods afforded nanoparticles rather than continuous films. Finally, thermal ALD of Ag has been achieved using [(fod)Ag(PEt$_3$)] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) with $BH_3(NHMe_2)$, affording films with a matte finish due to a rough microstructure.[7]

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

References

(1) Zilberberg, K.; Riedl, T. *J. Mater. Chem. A* **2016**, *4*, 14481-14508.

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(7) Mäkelä, M.; Hatanpää, T.; Mizohata, K.; Meinander, K.; Niinistö, J.; Räisänen, J.; Ritala, M.; Leskelä, M. *Chem. Mater.* **2017**, *29*, 2040-2045.

5:30pm AF2-MoA-17 A Novel Liquid Cocktail Precursor for Atomic Layer Deposition of Hafnium-Zirconium-Oxide Films for Ferroelectric Devices,

Akihiro Nishida, *Tsukasa Katayama, Takashi Endo, Yasutaka Matsuo,* Hokkaido University, Japan

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

References

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

ALD Fundamentals
Room Event Hall - Session AF-MoP
ALD Fundamentals Poster Session

AF-MoP-1 Atomic Layer Deposition of P-type Oxide Semiconductor Thin Films Using a Novel Precursor for Transistor Applications*, Sol-Hee Jo*, *Jung-Hoon Lee, Jimin Seo, Bo Keun Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

P-type oxide semiconductors are challenging to fabricate with high performance due to their low carrier mobility and concentration, unlike n-type oxide semiconductors. Despite these limitations, the development of p-type oxide semiconductors with reliable electrical performance is essential in the fields of Complementary Metal-Oxide-Semiconductor (CMOS) circuits, high-resolution displays, and monolithic three-dimensional (3D) integration technologies. We successfully deposited tin monoxide (SnO) by atomic layer deposition (ALD) using a novel precursor, and H_2O as a reactant. The SnO films exhibited an optical bandgap of ~ 2.5 eV and a refractive index of 2.4 or higher, which are typical optical properties of SnO. We confirmed that there were almost no impurities through X-ray photoelectron spectroscopy (XPS) measurement and the O/Sn ratio was ~ 1.0. Consequently, our experimental results showed that the novel Sn precursor is suitable for the ALD process. In addition, a p-type oxide semiconductor was applied as the channel layer in a thin-film transistor (TFT), resulting in the fabrication of a p-type oxide semiconductor TFT. These experimental results indicate that stable p-type devices can be fabricated and applied to future applications.

AF-MoP-2 Silicon Nitride Ald Process Using Diiodosilane and Hydrazine for Low Temperature Deposition*, Hayato Murata,* *Takuya Yoshikawa, Yoshifumi Wada, Hideharu Shimizu,* Taiyo Nippon Sanso Corporation, Japan

High quality ALD silicon nitride (SiN) is required for advanced device structure complexity. Especially, there is the demand for SiN films that are resistant to wet HF at deposition temperature below 500°C. Therefore, researchers around the world are studied silicon precursors and nitriding agents recently. For example, nitriding agent as high purity hydrazine (N_2H_4) is a promising nitrogen source for low temperature ALD nitride process due to its high reactivity [1-2].

Although we demonstrated SiN ALD using Si_2Cl_6 (hexachlorodisilane, HCDS) and N_2H_4 at 450°C, wet etching rate (WER) in dilute hydrofluoric acid (100:1 HF) was 150 Å/min. In this study, employing SiH_2I_2 (diiodosilane, DIS) instead of HCDS, we succeeded forming lower-WER SiN film at 450°C.

SiN ALD process was experimentally evaluated by delivering DCS/N_2H_4 or DCS/NH_3 to a hot-wall tubular reactor. SiN ALD using DIS/N_2H_4 or DIS/NH_3 were formed at 450-600°C.

In these results, SiN ALD using DIS/N_2H_4 were demonstrated even at 450°C although SiN ALD using DIS/NH_3 were unable to form thin films below 550°C.GPCs (growth per cycle) in DIS/N_2H_4 ALD were found to be 0.11-0.42 Å/cycle while those in DIS/NH_3 ALD were 0.26 Å/cycle at 600°C. These results indicate that N_2H_4, as higher reactive nitriding source than NH_3, has an effect on formation of SiN film at lower temperature.

In addition, WER in 100:1 HF of DIS/N_2H_4 film at 450-550°C was 92-12 Å/min. The WER of DIS/N_2H_4 film was lower than that of HCDS/N_2H_4 film. These indicates that the iodine atoms included in the DIS adsorbed on the substrate are readily removed during the nitriding process, since Si-I bond dissociation energy (E_d) is lower than that of Si-Cl (E_d of Si-I: 274 kJ/mol, E_d of Si-Cl: 392 kJ/mol). Thought phenomenon of N_2H_4 removing halogen through stronger nitridation than NH_3 is overserved [3], it is expected that the chlorine atoms in the absorbed HCDS remains as impurities in the SiN film. Therefore, the SiN film quality of DIS/N_2H_4 was superior to that of HCDS/N_2H_4.

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

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AF-MoP-3 Characterization of Novel Precursors for Improved ALD Performance in HfO_2 Films*, Dahyun Lee,* *Hohoon Kim, Sejin Jang, Seonah Kim, Dong-geun Lee,* Merck KGaA, Darmstadt, Republic of Korea*; Khang Ngo, Randall Higuchi,* Merck KGaA, Darmstadt

In atomic layer deposition (ALD), the selection of precursors is crucial, as they significantly influence film quality and the formation of thin films. It has been reported that the electrical characteristics of HfO_2 films improve when deposited at higher temperatures, creating a strong demand for Hf precursors that exhibit high thermal stability to facilitate high-temperature ALD of HfO_2. Currently, widely used precursors such as $CpZr(NMe_2)_3$ and $CpHf(NMe_2)_3$ (where Me = methyl and Cp = cyclopentadienyl) have limitations that have become evident as equipment and processes have evolved. Notably, $CpHf(NMe_2)_3$ exhibits a clear sign of thermal decomposition at 350°C. To address these challenges, we have designed a new series of precursors, termed the Helia series, which incorporates a Cp-based ligand. Experimental results demonstrate that the Helia series precursors possess superior thermal stability and reactivity, offering enhanced step coverage compared to conventional $CpHf(NMe_2)_3$ precursors, along with a wider ALD window. Specifically, the Helia series precursors have a wider ALD window than $CpHf(NMe_2)_3$, and unlike $CpHf(NMe_2)_3$, Helia-02 maintains an ALD window above 350°C. These findings indicate that the Helia series precursors not only outperform traditional materials but also hold great potential for advancing high-k dielectric applications. This poster discusses the development and performance evaluation of the Helia series precursors.

AF-MoP-4 Effect of Impurities in Trimethylaluminum on Conformality of Al_2O_3 Thin Film on Patterned Substrate Grown by ALD*, Shuya Ikemura,* *Kohei Iwanaga,* TOSOH Corporation, Japan

Aluminum oxide (Al_2O_3) is an important dielectric material for various applications including surface passivation, dynamic random-access memory (DRAM) and gate dielectric in complementary metal-oxide-semiconductors (CMOS) [1-3]. The trimethylaluminum (TMA) is one of the most studied precursor for producing Al_2O_3 films. Impurities in TMA with semiconductor grade seem to have been managed by mainly trace metal analysis. We focused on the impurities which are not precisely detected by the trace metal analysis and found that controlling their concentration to a certain level surprisingly affects the conformality of deposited Al_2O_3 films.

Two types of TMA precursors, [**TMA-1**] and [**TMA-2**], were prepared with different concentration of impurities. **TMA-1** contains the lower concentration of the impurities than **TMA-2**. Al_2O_3 thin films were deposited using each TMA precursor on line-and-space (L/S) patterned SiO_2 substrates with the aspect ratio of 20 using atomic layer deposition (ALD) apparatus. TMA was delivered by a self-evaporation method to an ALD reactor chamber with the assistance of Ar carrier gas. O_3 gas was also introduced as the oxygen source. In addition, diluent Ar gas was added. The atomic composition of the films was analyzed by means of X-ray photoelectron spectroscopy (XPS) after Ar^+ sputtering. Transmission electron microscope (TEM) was used to characterize film conformality.

Cross-sectional TEM images at the L/S pattern area demonstrated excellent step coverage of 96.5% for the film deposited utilizing **TMA-1** but smaller step coverage of 91.7% for that deposited utilizing **TMA-2** although the atomic composition of two samples were estimated to be no difference from the XPS measurements of the films deposited on planar substrates.

We have achieved to improve the Al_2O_3 film conformality by decreasing the impurities in TMA.

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AF-MoP-5 Thermolysis of Silicon Precursors for High-Temperature Atomic Layer Deposition Processes*, Tanzia Chowdhury,* *Okhyeon Kim, Hye-Lee Kim,* Sejong University, Republic of Korea*; Jung Woo Park,* Hansol Chemical Co., Ltd., Republic of Korea*; Won-Jun Lee,* Sejong University, Republic of Korea

The success of the atomic layer deposition (ALD) process is highly dependent on precursor selection, as only certain precursors are suitable for a given ALD process. While low process temperature is critical for temperature-sensitive devices, high-temperature ALD processes are often preferred for memory devices, such as 3D NAND flash. Elevated ALD process temperatures can improve thin film properties in such devices, including leakage current and wet etch rate [1]. High-temperature processes are typically performed in hot-wall reactors, where precursors are exposed to high temperatures for extended periods. Therefore, the thermal stability of the precursor is akey factor in enabling such processes. In this work, we investigate the thermolysis reactions of various silicon precursors using density functional theory (DFT) calculations for ALD of silicon oxide (SiO_2) and nitride.DFTserves as an effective tool for screening precursors. The selected silicon precursors include aminosilanes, chlorosilanes with Si–Si bonds, and heteroleptic compounds. Silicon tetrachloride ($SiCl_4$) was also studied as a reference due to it being the most basic silicon precursor that had an activation energy of 4.92 eV for thermolysis. The thermal stability of these precursors, predicted by DFT, was validated by the maximum ALD temperature determined experimentally. $Si(NMe_2)_3H$ was the most stable among the aminosilane precursors studied, with an activation energy of 2.49 eV. DFT also predicted that CH_3SiCl_3had sufficient thermal stability with an activation energy of 3.40 eV. Experimental results showed that the maximum temperatures for SiO_2 ALD were 750 °C for CH_3SiCl_3 and 600 °C for $Si(NMe_2)_3H$, which were consistent with their respective thermolysis predictions from DFT. This work demonstrates that DFT can effectively predict the thermal stability of ALD precursors, which will accelerate the selection of suitable precursors, especially athigh process temperatures.

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AF-MoP-6 On an Initial Incubation Process of Thermal ALD Pt on ALD Al_2O_3 Measured by Temperature Stabilized In-line QCM

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The initial process of a thermal ALD of Pt, with precursor $MeCpPtMe_3$ (abbr. as CpPt) and reactant O_2, on an ALD Al_2O_3 surface was monitored by an in-line QCM. A crystal with Tturnover of 285ºC or 240 ºC was used, and temperature profile around the crystal was optimized for use in a wide temperature range of 200-285ºC. A Quartz glass tube reactor of 300mm (L) × 40mm (D) was used. Reactant gases O_2 and H_2O were supplied by a measuring bottle of $10cm^3$ capacity, which limits the number of injected molecules to 2×10^{13}.

Fig. 1 shows QCM profiles derived from 40 cycles of CpPt /O_2 at 265ºC, employing the crystal with Tturnoverof 285ºC (Inficon 1060). Prior to this, AlOH surface is prepared by 40 cycles of TMA/H_2O.

At the 1st CpPt injection, a rapid frequency increase, a = 1.83Hz, appears as found in Fig. 2. Utilizing the step frequency change in TMA/H_2O cycle, k = 3.8Hz, and an atomic mass of -Al-OH unit on the surface[1)], q = 44, a corresponding atomic mass reduction Δm (CpPt n = 1) is estimated as $(a/k)q$ = 21. Before the 1st CpPt injection, ideally no atomic Pt bond exists on the initial surface of the Al_2O_3 layer. Thus, a suggests the removal of a surface bound OH by CpPt, resulting in the retention of the same number of vacancies as the original AlOH sites. A frequency decrease, b = 0.48Hz, emerges subsequent to the peak of a, which is possibly related to a refill process of the vacancy with OH molecules and/or contaminated O_2 from the upper stream region of the reactor.

At the 1st O_2 injection, a quick frequency drop, c = 1.42Hz, is observed. The atomic mass increase Δm (O_2 n = 1) is $(c/k)q$ = 16.4, which suggests the adsorption of O and OH. Subsequent CpPt injection induced both PtO_x nucleation and OH removal on the AlOH surface. The net frequency difference during the first cycle, d (n = 1), is 0.06Hz. Refer to frequency decrease in the stabilized 40th cycle of CpPt (= 15.8Hz/cycle), the mass gain in the 1st cycle, i.e. Pt nucleation, is estimated as 0.38% of full coverage Pt surface. In the 2nd CpPt cycle, d (n = 2) is 0.43Hz, and the mass gain increases by 0.43/15.8 = 2.72% .

As the cycle repeats, a decreases and becomes almost zero at the 12th CpPt injection, indicating that no AlOH unit remains on the surface. The accumulated value of d from the 1st to 12th cycles is 14.62Hz, close to 15.8Hz of the frequency gain in the 40th CpPt cycle. In conclusion, the cycle step where no AlOH remains on the surface and the frequency increase a becomes zero can be defined as the end point of island growth.

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AF-MoP-7 Oxide Film ALD Using Oh Radicals Generated by Mixing Pure Ozone Gas with Hydrogen-Included Molecular Gas Over 200ºC

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For the deposition of oxide films using ALD, various oxidizing gases such as water, oxygen plasma, and ozone are used. These oxidizing gases are selected according to the required film qualities, which are coverage of trenches with high aspect ratios, electrical properties, and high productivity by batch processing.

We have reported the quality of oxide films such as Al_2O_3 by ALD using high-concentration pure ozone gas (≥80 vol%) as the oxidizing source [1].Pure ozone gas has a longer half-life in the gas phase than conventional ozone gas (<10 vol%), so we have confirmed that Al_2O_3 can be formed in trenches with high aspect ratio(> 1500) [2]. Furthermore, pure ozone can produce OH radicals, which have higher oxidation reactivity than ozone, by mixing with ethylene gas (OER method). It has been confirmed that ALD using OER (OER-ALD) has improved film quality such as GPC and insulation of Al_2O_3 films at 150℃ or less compared to ALD using pure ozone and is equivalent to oxygen plasma [1]. However, the range of applicable temperature of OER-ALD is lower than the ALD window temperature range (≥200℃) of many precursor species. In the case of OER-ALD, ozone and ethylene are highly reactive even at low temperatures, so gas mixing is required near the substrate using a shower head[3]. Increasing the substrate temperature requires more precise mm range subtle gap control between the shower head and the substrate due to increased reactivity of the gases involved and the short lifetime of radicals in-situ generated. Therefore, it becomes difficult to adjust the dimensions of the OER-ALD equipment configuration.

In this presentation, we will discuss the method of the OH radical generation using pure ozone gas and ethylene alternative gas above 200℃. This gas has lower reactivity with ozone than ethylene and must contain hydrogen atom in the molecular structure. Among the several gas species candidates to replace ethylene, water vapor (H_2O) is expected to be effective in reducing carbon residues in the film because it does not contain carbon. We will demonstrate the HfO_2 film qualities using this OH radical ALD.

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AF-MoP-8 Novel Indium Precursor with Improved Physical Properties and ALD Window for Atomic Layer Deposition of Indium Oxide

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Indium gallium zinc oxide (IGZO) is an important film for thin-film transistors (TFT) due to its excellent electrical and optical properties. (1) Precursor selection is crucial for ALD of the separate indium, gallium and zinc precursors as they all need to be deposited at the same temperature. Currently trimethylindium (TMI) is commonly used due to having a similar ALD window as other common precursors for gallium and zinc oxide. (2) TMI has limitations as a precursor because it is a solid at room temperature as well as being pyrophoric.

A new precursor has been developed for indium oxide deposition that is non-pyrophoric and a liquid at room temperature. Through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) we confirmed liquid phase at room temp, vapor pressure (1 Torr at 40C) and decomposition temperature showing good performance for an ALD precursor. Deposition testing was completed using this new In precursor and ozone showing an ALD window for In_2O_3 from 275C-325C. Linear growth was observed and a dep rate of 0.7A/cycle was found in the ALD window. The findings show a promising Indium precursor for IGZO deposition.

AF-MoP-9 Atomistic Modeling Methodologies for Atomic Layer Deposition*, **Yong-Ju Kang,*** Synopsys Korea Inc., Republic of Korea*; Suresh Kondati Natarajan,* Synopsys Inc., Denmark*; Rafshan Ul Atik,* Synopsys India Pvt. Ltd., India*; Jess Wellendorf, Søren Smidstrup,* Synopsys Denmark ApS, Denmark

Atomic layer deposition (ALD) is a thin-film deposition method, which grows one atomic layer sequentially with precise control of thickness and precursor chemistry. It means that understanding atomistic nature of precursors and their surface reactions became more important than other conventional chemical vapor deposition method. Atomistic simulation methodologies are powerful tools for analyzing surface reactions and elucidating complex dynamical processes of ALD at atomic scale, given process conditions. In this work, we will present various atomistic modeling approaches for atomic layer deposition (ALD) by using QuantumATK software [1,2] developed by Synopsys. In thermochemical analysis, Gibbs free energy of surface reactions calculated using the density functional theory (DFT) and the energy of reactants and products compared according to process temperature and partial pressure to find favorable surface reactions. Using the kinetic approach, deposition rate was obtained by calculating activation barrier of surface reaction and solving equation of time dependent surface coverage. In dynamical approach of reactions, molecular dynamic simulations impacting precursor molecule onto the film surface performed to understand dynamical process of surface reaction. In this approach, with generation of explicit atomic structure of the surface and reaction products, reaction properties such as probabilities of events and sticking coefficient were extracted by using classical or machine learned force fields [3,4].

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AF-MoP-10 Unraveling the Influence of Substrate Surface and Temperature on Microstructural Evolution of Crystalline MoS_2 in Atomic Layer Deposition*, **Seung Ho Ryu**, Seong Keun Kim,* Korea University, Republic of Korea

In this study, we examine the atomic layer deposition (ALD) growth behavior of crystalline MoS_2 films on various substrates, including SiO_2, mica, and Al_2O_3, at deposition temperatures of ≥ 650 °C. The results show that the substrate surface energy and temperature significantly influences the MoS_2 growth dynamics, affecting the layer nucleation, surface morphology, and growth rate. High temperatures generally favor a stepwise growth pattern with a step size of one monolayer; however, the substrate surface energy distinctly affects the grain size and crystallinity. MoS_2 growth on mica, which has the lowest surface energy, results in larger, highly crystalline triangular grains and enables multilayer growth, whereas Al_2O_3, which has the highest surface energy, produces smaller, less crystalline grains. Temperature elevation further enhances the lateral grain expansion and crystallinity, especially on Al_2O_3 substrates with higher surface energies. By tailoring the substrate surface and deposition temperature, the key pathways for optimizing MoS_2 ALD growth are highlighted with the aim of enhancing the film uniformity and quality for nanoelectronic applications. This study provides critical insights into the ALD parameters that govern the growth of crystalline MoS2 with implications for advancing scalable, high-performance 2D materials.

AF-MoP-11 Novel Alkoxy-Bridged Silicon Precursor for Plasma Enhanced Chemical Vapor Deposition of Low-k SiCOH Spacer Thin Film*, **Jongryul Park**, Sooyong Jung, Seokhee Shin, Yongjoo Park,* SK Trichem, Republic of Korea

Low dielectric constant(low-k) materials are essential for various applications due to their unique material properties and play a broad role in semiconductor devices. Dynamic random access memory(DRAM) has continued to shrink to gain higher data storage capabilities. At the same time, its manufacturing will face many challenges at advanced technology node, such as the decreased retention time and the insufficient sensing margin. Reducingthe parasitic capacitance between the bit line(BL) and the storage contact is one method to block the leakage of the cell is the solution to make up the decreasing of retention time and solve the insufficient sensing margin.[1] To prevent the increase of parasitic capacitance as the cell sizes decrease, a low-k material be used between the BL and the storage contact. In addition, it should have high density and good resistance properties to etching for subsequent processes. Previous studies have investigated the properties of the silicon oxycarbonitride(SiOCN, k=5.2). However, they are not suitable for low-k materials due to their relatively high dielectric constant.[2]

In this study, a new alkoxy-bridged silicone precursor with low viscosity and good volatility was developed to form a SiCOH-based low-k spacer materials. The SiCOH thin film was formed through a PECVD process using O_2 plasma at 400℃ on the new silicon precursor. The characteristics of the formed thin film were confirmed through the evaluation of k-value, reflective index(R.I.), density and wet etch rate. It has the characteristics of a low-k spacer material suitable for application to next-generation semiconductor devices.

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AF-MoP-12 High Temperature Atomic Layer Deposition of Hafnium Oxide Film using Novel Liquid Hf Precursor Deposition*, **Kim Daeyeong**,* SK Trichem, Republic of Korea*; Oh Jieun, Lee Seo-Hyun, Kim Woo Hee Kim,* Hanyang University, Korea*; Park Yongjoo,* SK Trichem, Republic of Korea

Hafnium oxide (HfO_2) is a high-k dielectric material that has contributed to the scaling of memory and logic devices, and is also explored for storage class memories. As memory devices become more complex, conformal deposition of HfO_2 films on nano-sized 3D structures is increasingly important. Deposition temperature plays a key role in achieving high-quality films, as low-temperature processes may hinder property preservation due to thermal budget constraints in 3D integration. Although low-temperature deposition is desirable, high-temperature processing is crucial for optimizing the HfO_2 film’s high-k properties. Therefore, a process capable of depositing HfO_2 films at elevated temperatures is necessary.[1]

In ALD of HfO_2, various precursors have been explored, with thermal stability being crucial to achieving high-quality films. Metal halides like $HfCl_4$ offer excellent stability but produce corrosive by-products and introduce chlorine impurities. Alkylamides like $Hf(NEtMe)_4$ provide high growth rates but suffer from limited thermal stability and impurity incorporation. In particular, $(CpR)Hf(NMe)_3$ (R = H, Me) provides an ALD window of 250–350 °C for HfO_2 growth, offering good crystallinity and stability at this temperature range. However, the relatively low ALD window temperature makes it unsuitable for high-temperature processes. [2]

Herein, we developed a novel liquid hafnium precursor with low viscosity, good volatility, and thermal stability. Using this precursor, we were able to achieve a high-temperature ALD window for HfO_2, ranging from 300 to 400 °C. The growth per cycle (GPC) during this process was 0.7 Å/cycle. X-ray reflectivity (XRR) was used to measure film density, and grazing incidence X-ray diffraction (GIXRD) was employed to investigate the crystalline structure of the films. Electrical characterization of the films was performed through leakage current density-electric field (J-E), interface trap density (D_{it}), and capacitance-voltage (C-V) measurements.

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AF-MoP-13 Analysis of Plasma Characteristics and Substrate Damage Using a Dual-Frequency PE-ALD Process with 13.56 MHz and 100 MHz*, **Da-Eun Bae**, Hyung Min Kim, Jae Yeon Han, Jae Ho Choi, Jae Hack Jeong,* CN1 Co., Ltd., Republic of Korea

Compared to other deposition methods, ALD processes are widely applied in mass production due to their high step coverage, atomic-level thickness control, and uniform film deposition. However, thermal ALD requires high temperature (>400℃) to achieve high-quality properties when depositing nitride films such as SiN_x, AlN, TiN, and TaN. This has led to the application of plasma-enhanced ALD (PE-ALD). It offers enhanced reactivity and higher deposition rates, even at low temperatures. However, it also presents several technical challenges, including plasma-induced substrate damage and limited step coverage in increasingly thinner and deeper structures. To address these issues, the use of very high frequency (VHF) plasma is required.

We have studied plasma characteristics and substrate damage during the deposition of silicon nitride (SiN_x) films using a PE-ALD process at low temperatures (≤200°C) with very high-frequency plasma. In this process, the use of 100 MHz alone resulted in insufficient discharge and poor uniformity due to standing wave effects, and thus a dual-frequency approach was applied by combining 13.56 MHz with 100 MHz to improve plasma stability. Plasma characteristics, such as electron temperature (T_e), ion flux, and ion density, were characterized using a Langmuir probe. Plasma-induced substrate damage was examined using TEM, and film thickness and refractive index (RI) were measured using ellipsometry.

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AF-MoP-14 High-Temperature, High-Growth Rate Atomic Layer Deposition of Silicon Oxide Thin Films Using a Novel Precursor*, **Changgyu Kim**, Mi-Soo Kim, Okhyeon Kim, Jihwan Lee,* Sejong University, Republic of Korea*; Seunggyun Hong, Byung-Kwan Kim, Jin Sik Kim, Wonyong Koh,* UP Chemical Co., Ltd., Republic of Korea*; Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

As the number of layers in three-dimensional (3D) vertical NAND devices continues to increase, so does the aspect ratio of the channel holes. Atomic layer deposition (ALD) is essential to form dielectric thin films with excellent step coverage in these high-aspect-ratio structures. Since higher process temperature improves the physical and electrical properties of ALD dielectric films, there is a growing demand for high-temperature thermal ALD processes in 3D NAND fabrication. In a previous study, we demonstrated the feasibility of a novel silicon precursor, HTS-1, for high-temperature ALD applications [1]. We achieved high growth rates exceeding 2.5 Å/cycle at 600–800°C, more than two times higher than $SiH(NMe_2)_3$. We also observed excellent step coverage at 750°C. However, the maximum temperature for SiO_2 ALD using HTS-1 was not determined, and the detailed investigation of film properties over different process temperatures was lacking. In this work, we systematically investigated the SiO_2 film deposited by alternating exposure to HTS-1 and ozone at different temperatures. First, we determined the saturation doses of precursor and ozone. Then, we analyzed the growth rate as a function of deposition temperature to determine the maximum ALD temperature, which was confirmed by evaluating the step coverage at different deposition temperatures. Finally, we analyzed the physical and electrical properties of the deposited film at different temperatures, including composition, impurities, shrinkage, and leakage current. The properties of SiO_2 films prepared with HTS-1 were also compared with those prepared with $SiH(NMe_2)_3$, providing insight into the advantages of the novel precursor for high-temperature ALD.

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AF-MoP-15 Development of New Group 3 Metal and Lanthanide Precursors with Volatility and Thermal Stability for ALD*, **Yongmin Go**, Bo Keun Park,* 141, Gajeong-ro, Yuseong-gu, Republic of Korea

Group 3 metals and lanthanide metal oxides are known for their high permittivity and wide band gaps, making them ideal materials for MOSFETs and DRAMs. Various thin film deposition techniques are employed in the production of metal oxide films, among which atomic layer deposition (ALD) stands out due to its ability to produce high-quality films, self-limiting growth, and precise control over film thickness.

To carry out the ALD process, the use of ALD precursors is essential. These precursors must possess volatility, thermal stability, and high reactivity with the reactants, making the development of new ALD precursors with these characteristics of great importance. However, the size of Group 3 metals varies depending on the specific metal, and an appropriate ligand must be used.

In this work, we have developed a new Group 3 metal novel ALD precursor and analyzed its suitability for use as an ALD precursor. The characteristics of the newly synthesized Group 3 metal precursors were confirmed through various analysis methods, such as NMR, EA, TGA, and vapor pressure. Among them, the new lanthanum precursor was confirmed to form a thin film through the ALD deposition process.

Additionally, we proposed an ALD process for La_2O_3 using the new lanthanum precursor and compared it to the commonly used $La(^iPrCp)_3$ precursor. By processing at high temperatures with the new lanthanum precursor, we successfully obtained La_2O_3 thin films with excellent crystallinity, higher density, and improved leakage current characteristics. These results suggest that the new precursors we developed are promising candidates for the formation of metal oxide thin films through ALD and deposition processes.

AF-MoP-16 Exploring Ultrathin SnO_2 Films via Atomic Layer Deposition for Facilitating the Formation of the Rutile TiO_2 Phase*, InHwan Baek, **YooHyeon Jung**, InHong Hwang,* Inha University, Republic of Korea

Tin dioxide (SnO_2) is a chemically stable and conductive oxide material that is currently being investigated for potential application in DRAM electrodes, driven by the increasing demand for semiconductor scaling. The practical limitations of increasing capacitance by continuously reducing the thickness of the dielectric film have led to a growing need for new dielectric materials. Among these materials, rutile-TiO_2 (k > 100) is particularly noteworthy. However, synthesizing a high-k rutile phase requires high-temperature processes exceeding 700 ˚C, which are incompatible with the CMOS process. To overcome this challenge, the rutile structure of SnO_2 can be employed as a seed layer, enabling the low-temperature synthesis of rutile TiO_2 via local epitaxy. In this study, we developed a method for synthesizing rutile SnO_2 by atomic layer deposition (ALD) using H_2O_2 as co-reactant, which facilitates more effective ligand removal from Sn precursor by enhanced byproduct exchange. The resulting films exhibit superior physical, chemical, and electrical properties, ensuring their suitability for advanced dielectric integration. This approach eliminated the need for ozone, which has the potential to oxidize the DRAM bottom electrodes. We believe that the SnO_2 seeds layer can be utilized to fabricate the next generation of dielectric films, rutile TiO_2, regardless of bottom electrode type.Acknowledgment: This work was supported by Korea Institute for Advancement of Technology(KIAT) grant funded by the Korea Government(MOTIE) (RS-2024-00409639, HRD Program for Industrial Innovation)

AF-MoP-17 Novel ALD Indium Precursor for In_2O_3 Thin Film Fabrication*, **Dong Hyeon Bang**, Bo Keun Park, Yongmin Go, Sunyoung Shin, Ji Yeon Ryu,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Indium oxide thin films are utilized in various applications, including catalysis, displays, gas sensors, and transistors. To fabricate these metal oxide thin films, vapor-phase deposition techniques such as Metal-Organic Chemical Vapor Deposition (MOCVD), Physical Vapor Deposition (PVD), and Atomic Layer Deposition (ALD) are commonly employed. Among these techniques, ALD offers the advantage of precise control over film thickness by adjusting the number of deposition cycles. It also enables the formation of high-quality thin films with low contamination compared to other deposition methods. To leverage these advantages of ALD, precursors with high volatility and thermal stability are required. In this study, we synthesized novel heteroleptic indium precursors by introducing thermally stable enaminolate ligands to $InMe_2Cl$. The molecular structures of compounds **1**–**3** were confirmed using X-ray crystallography (XRD), which revealed that all three compounds possess dimeric structures and adopt distorted trigonal bipyramidal geometries. Thermogravimetric analysis (TGA) indicated that compounds **1**–**3** exhibited single-step weight loss behavior, with non-volatile residues at 500 °C measured as 24% for **1**, 30% for **2**, and 20% for **3**. Additionally, it was observed that the sublimation temperatures of compounds **1**-**3** ranged from 30 to 35 °C at a pressure of 0.65Torr. The thermal properties and vapor pressures of compounds **1**-**3** indicate their potential suitability as precursors for atomic layer deposition process.

AF-MoP-18 Optimization of ALD Processes and High-Quality Thin Film Formation Using the Liquid Aluminum Precursor 1,5-Dimethyl-1-Alumina 5-Azacyclooctane, *Sangick Lee, **Sanghun Lee**, Yunsik Park, Sejin Jang, JoongJin Park, Sangyong Jeon, JunHee Cho,* DNF, Korea (Democratic People's Republic of)

This study introduces an atomic layer deposition (ALD) process utilizing the liquid aluminum precursor 1,5-Dimethyl-1-Alumina 5-Azacyclooctane (hereafter referred to as DMACO), designed to meet the demands of advanced integration and miniaturization in semiconductor devices. To achieve higher DRAM capacitance, precise control over the amount of Al_2O_3 in the dielectric layer is crucial; however, the TMA precursor's high deposition rate limits this control. A new ALD precursor with a significantly lower deposition rate, while maintaining film quality and cost efficiency, is needed. DMACO exhibits a stable ALD window in the temperature range of 350–550℃, with superior thermal stability and lower impurity levels compared to TMA.DSC analysis revealed that TMA thermally decomposes at approximately 237℃, while DMACO decomposes at around 405℃ using the same method.The deposition rate of TMA was approximately 0.87–2.27 Å/cycle at 350–550℃, whereas DMACO showed a lower deposition rate of about 0.77–1.08 Å/cycle under the same conditions. Despite this lower deposition rate, Al_2O_3 films deposited on Si substrates via the ALD process using DMACO exhibited high uniformity and excellent step coverage, showing performance comparable to high-k dielectric materials deposited with TMA. Furthermore, XPS and TEM analyses confirmed the formation of high-quality thin films with minimal carbon (C) and other impurities. This presentation will delve into the thermal properties of DMACO (TGA/DSC), deposition rate trends, optimization of ALD process conditions, and the physical and chemical characteristics of the deposited films.

AF-MoP-19 Low-Resistivity Molybdenum Thin Films Deposited by ALD Using Molybdenum(0) Organometallic Compounds and Iodine-Containing Reactant, *Sang Ick Lee, **Ji Hyeon Youn**, Yo Han Jo, Won Mook Chae, Sang Yong Jeon, Joong Jin Park, Se Jin Jang,* DNF Co., Ltd., Republic of Korea

Selecting suitable candidates for interconnects and metal contacts has become increasingly challenging due to the exponential rise in metal resistivity at reduced pitches. Molybdenum (Mo) has emerged as a promising alternative to traditional metals like copper and tungsten, thanks to its low electrical resistivity and long electron mean free path. However, the deposition of Mo metal films typically requires high temperatures (600℃) and inorganic solid precursors, which can restrict its applicability. To address this limitation, a low-temperature deposition process is needed, which can be achieved by introducing an iodine-containing reactant.

Studies have shown that iodine acts as a catalyst, enhancing the growth rate and promoting denser, more uniform nucleation. Additionally, when iodine-containing species were briefly introduced during deposition, nucleation improved significantly, resulting in the formation of smoother films. [1,2] These iodine sources are also believed to help improve electrode leakage characteristics by reducing surface roughness.

In this study, the reactivity of specific reactants containing molybdenum(0) organometallic compound and iodine-containing reactant was investigated based on literature findings, and ALD deposition was carried out accordingly. The ALD process was analyzed to confirm key behaviors such as saturation, process window, and linearity. The deposited film was identified as an Mo film through characterization techniques, including XRD, XPS, and SIMS. Furthermore, evaluations on a patterned wafer verified its step-coverage and bottom-up characteristics.

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AF-MoP-20 Valence-state Controlled Growth of P-type Tin(II) Monoxide Films by Atomic Layer Deposition using a Novel Sn Precursor, *Jeong Hwan Han, **Jeong Eun Shin**,* Seoul National University of Science and Technology, Republic of Korea; *Heesun Kim, Bo Keun Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Tin monoxide (SnO), in its divalent oxidation state, exhibits excellent p-type conductivity due to the valence band maximum structure formed by the hybridization of Sn 5s and O 2p orbitals, making it a promising candidate for p-channel thin-film transistors (TFTs) [1]. However, physical vapor deposition methods such as evaporation and sputtering often struggle to achieve single-phase SnO films with precisely controlled Sn/O composition while minimizing the formation of undesired Sn or SnO_2 phases [2]. To address this issue, atomic layer deposition (ALD) has been explored to produce high-quality crystalline SnO films at low temperatures. Previous ALD SnO processes utilizing various divalent Sn precursors have been limited by poor crystallization within a narrow temperature rangedue to low precursor reactivity and thermal stability.

In this work, we developed an ALD process for SnO thin films using a novel divalent Sn amide precursor with a low sublimation temperature and high thermal stability. Thermogravimetric analysis revealed a single-step sublimation curve, confirming the excellent volatility and stability. The self-limiting ALD characteristics were verified by varying the Sn precursor and H_2O pulse times. The deposited SnO films were characterized using SEM, XRD, XPS, and UV-Vis, confirming the formation of pure andcrystalline SnO film. ALD SnO based TFT demonstrated excellent switching performance, exhibiting a field-effect mobility of 3.68 $cm^2/V\cdot s$, a sub-threshold swing of 4.94 V/dec, and an on/off current ratio of 2.74×10^3.

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AF-MoP-21 Synthesis and Characterization of Ge and Sn ALD Precursors with Aminoketone Ligands, ***Chang Min Lee**, Bo Keun Park, Heesun Kim, Ji Min Seo, Yongmin Go,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Seung Uk Son,* Sungkyunkwan University, Korea; *Ji Yeon Ryu, Taek Mo Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Thin films, with thicknesses ranging from nanometers to micrometers, can be produced through various physical or chemical methods. Atomic Layer Deposition (ALD) is particularly valued for its ability to deposit uniform thin films, where precursor selection plays a critical role in determining process success. For ALD, precursors must exhibit thermal stability, chemical reactivity, and produce volatile by-products. Among group 14 elements, germanium (Ge) and tin (Sn) have garnered attention due to their superior electrical and optical properties. Their oxides, GeO_2 and SnO_2 , have been extensively studied in thin film applications. In this study, we synthesized novel Ge and Sn precursors suitable for ALD and characterized their properties. $GeCl_2$ -dioxane and $Sn(btsa)_2$ were reacted with ligands dmadma (2-(dimethylamino)-N,N-dimethylacetamide) and dmadmb (1-(dimethylamino)-3,3- dimethylbutan-2-one). The resulting complexes formed stable five-membered rings, which effectively filled vacant coordination sites and prevented oligomerization. The synthesized compounds were thoroughly characterized using NMR, FT-IR, elemental analysis (EA), TGA, and XRC. All compounds exhibited high volatility and thermal stability, indicating their potential as promising precursors for ALD applications.

AF-MoP-22 M(II) (M = Ni, Cu, Ge, Sn) ALD Precursors Using N-tert-butylformamide Ligand, ***Mi Jeong Kim**,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Ji Min Seo,* korea research Institute of Chemical Technology (KRICT), Republic of Korea; *Heesun Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Yongmin Go,* korea research Institute of Chemical Technology (KRICT), Republic of Korea; *Seung Uk Son,* Sungkyunkwan University, Korea; *Ji Yeon Ryu, Taek-Mo Chung, Bo Keun Park,* korea research Institute of Chemical Technology (KRICT), Republic of Korea

Atomic layer deposition (ALD) has become an essential technology in advanced applications that require uniform and precise thin film deposition. The success of the ALD process depends on the selection of appropriate precursors. Accordingly, we conducted research to develop various M(II) precursors. We synthesized $[Ni(tbfa)_2]_2$ (**1**), $[Cu(tbfa)_2]_2$ (**2**), $Ge(tbfa)_2$ (**3**), and $Sn(tbfa)_2$ (**4**) complexes using N-tert-butylformamide (tbfa) ligands, and characterized them by various analytical techniques, including NMR, FT-IR, elemental analysis, and thermogravimetric analysis. In particular, complex 4 showed the highest volatility and stable thermal properties in the TGA results, and thus could be expected to be used as a good ALD precursor.

AF-MoP-23 Reaction Pathway of Copper Atomic Layer Deposition via Time-of-Flight Mass Spectrometry*, Camilla Minzoni, Caroline Hain, Krzysztof Mackosz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; Andreas Werbrouck,* Thin Film Coatings and Materials Electrochemistry Lab, University of Missouri-Columbia, Missouri, USA*; Carla Frege, **Bensaoula Abdel,*** Tofwerk AG, Thun, Switzerland*; Patrik Hoffmann, Ivo Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Time-of-Flight Mass Spectrometry (ToFMS) has emerged as a powerful analytical technique for unraveling the complex reaction mechanisms occuring during Atomic Layer Deposition (ALD), particularly in the challenging field of copper thin film fabrication. Thanks to its unique advantages in terms of high sensitivity, high resolving power, rapid data acquisition, and ability to simultaneously detect species across a wide mass range, ToFMS enables real-time tracking of surface reactions volatile byproducts.

In this study, in-situ ToFMS monitoring was employed to investigate the ALD process of copper, using dehydrated Cu(hfac)$_2$ as the Cu source and diethylzinc (DEZ) as the reducing agent. Until now, no experimental proof of the occurring surface reaction mechanism was attempted according to published literature.

Lee et al. [1] previously proposed a transmetalation reaction using an analogous copper complex and DEZ. The mechanism involves a ligand exchange step between the copper complex and DEZ, leading to the formation of the volatile byproduct Zn(hfac)$_2$, along with the generation of copper alkyl surface species. These copper alkyl species rapidly undergo reductive elimination, producing copper metal and butane (C_4H_{10}) [2].

Alternately, Elliott et al. [3] proposed another possible mechanism, involving a half ligand exchange reaction. This second pathway results in the formation of EtZn(hfac) and copper alkyl species, which subsequently react to yield copper metal and butane

In situ ToFMS monitoring enabled real-time detection of the expected volatile surface reaction products from both the transmetalation and half-ligand exchange mechanism with varying proportion in the ALD half-cycles of the copper precursor Cu(hfac)$_2$ and the reducing DEZ agent. By identifying the parent peaks of Zn(hfac)$_2$ and EtZn(hfac), along with their specific fragmentation pathways, ToFMS provided the first experimental validation of both reaction mechanisms under vacuum ALD conditions.

The combination of ALD and ToFMS is therefore proving to be a powerful method for a depth understanding of complex ALD reaction mechanisms, an insight that would be challenging to obtain through other means.

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AF-MoP-24 Bimetal Thin Film Deposition Using Novel Organometallic Dinuclear RuCo Complex*, **Kazuaru Suzuki**, Tomohiro Tsugawa, Subhabrata Das, Yohei Uchiyama, Ryosuke Harada, Hirofumi Nakagawa,* Tanaka Precious Metal Technologies Co. Ltd.,, Japan

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Thin films composed of multiple metal elements are attracting attention. In addition to those exhibiting catalytic activity or electro-magnetic properties, in the field of advanced semiconductors, multiple types of metal thin films are being studied for barrier / liner films for Cu wiring [1, 2]. In the production of such film, it is a common method to perform repetition of film formation operations according to the kinds of metal element, but it is complicated to perform film formation under different conditions for each metal. Further, it is difficult to deposit a smooth continuous film while having an extremely thin film thickness. In this study, we report the results of bimetal thin film deposition in a single process using novel organometallic dinuclear RuCo complex as a precursor.

Novel RuCo complexes containing several organic ligands were synthesized. Based on the results of TG measurement, the complex with high volatility and thermal stability was selected and used as a raw material for film formation. As the intial evaluation, CVD deposition test was performed on Si and SiO$_2$ substrates. The film formation was controlled at substrate temperatures ranging from 300 to 400 ºC. When the films were formed in nitrogen atmosphere, high-resistance films containing impurities were obtained, but in the hydrogen atmosphere, the low-resistance metal films were obtained. From the results of SEM, it was confirmed that the flat and continuous films with no agglomeration or particles were obtained. In addition, the EDS measurement results showed that Ru and Co elements in the film were uniformly distributed without aggregation.

We have developed the novel precursor that can produce a uniform bimetal film containing Ru and Co elements by the deposition process with single precursor. Since an extremely thin and continuous film is required for use in the barrier/liner film of Cu wiring, the development of an ALD process is more necessary in the future.

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AF-MoP-25 Atomic Layer Deposition of Composition Engineered Nitrogen-Doped SnOX Films for Enhanced Performance of Thin-Film Transistor*, Han Jeong Hwan, **Lee Hyun Hak**, Shin Jeong Eun, Lee Na Yeon,* Seoul National University of Science and Technology, Republic of Korea

Tin oxide (SnO$_x$, x = 1,2) has been widely used in various applications, including thin-film transistor (TFT) channel layers, solar cells, and transparent electronic devices, due to its excellent electrical and optical properties. By controlling stoichiometry, tin oxide can achieve n-type SnO$_2$ and p-type SnO semiconductors. However, the formation of unintended intrinsic defects such as oxygen vacancy and tin vacancy can degrade device stability and complicate carrier concentration control. To address this issue, studies on anion doping, such as nitrogen, have been explored. However, Nitrogen-doped oxide semiconductors produced by sputtering processes face challenges in controlling doping concentrations. In contrast, atomic layer deposition (ALD), which enables atomic-scale deposition through self-limiting reactions, allows for precise doping concentration control via a super-cycle approach.

In this study, nitrogen (N)-doped SnO$_x$ films were grown using thermal ALD, incorporating alternating ALD SnO$_x$ and SnN$_x$ sub-cycles. By varying the sub-cycle ratio of SnO$_x$:SnN$_x$, the nitrogen concentration in N-doped SnO$_x$ film was precisely adjusted. The influences of nitrogen doping concentration on crystallinity, surface morphology, chemical states, and optical and electrical properties were systematically analyzed using XRD, SEM, AFM, XPS, and UV-vis spectroscopy. Finally, the electrical performance of ALD N-doped SnO$_x$ TFTs were evaluated depending on the nitrogen doping levels.

Acknowledgments

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AF-MoP-26 Atomic Layer Deposition of Molybdenum Using a Dual-Purpose Molybdenum Precursor for Advanced Metallization*, **David Mandia**, Matthew Griffiths, Youness Alvandi, Arya Shafiefarhood,* Lam Research Corporation

The resistivity increase with decreasing width of interconnect lines is a major challenge for the continued downscaling of integrated circuits. As middle-of-line (MOL) metal interconnects in advanced logic devices scale down to the sub-2 nm node with an associated reduction in the overall current-carrying cross-sections, the effects of specular electron scattering at grain boundaries[1] or impurities like carbon/oxygen become tremendously amplified. As we inflect to a Molybdenum (Mo)-based metallization solutions in our customer integration schemes (and away from Cobalt (Co), Ruthenium (Ru), and tungsten (W)), the previously mentioned challenges remain the same. Our typical integration schemes for S/D or contact metallization are based on recessed features with ALD/CVD Mo gap-fill within (i) inherently selective structures with a barrierless W via bottom or (ii) structures with a conformal diffusion barrier on, for example, a metal silicide/Si. To improve upon previous approaches to gap-fill of structure (i), which were based on an oxygen-containing Mo precursor, we employed an oxygen-free, halide-containing Mo precursor ($MoX_a(L)_b$). This allowed for a cleaner, bottom-up (selective) growth profiles with an oxygen-free Mo-W interface. As will be shown in various analyses (e.g., PED), we obtain single-grain Mo in most (>90%) vias of ourLam-internal test vehicle structures due to the lack of grain boundary formation,which tends to form if there are significant Mo precursor and feature sidewall interactions. Due to its oxophilicity (i.e., its high affinity to oxidize to MoOx), Mo is a challenging metal from both a processing and precursor design point of view. Herein we leverage the various deposition and etching properties of a $MoX_a(L)_b$ precursor and its applications in various metallization schemes.

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Keywords: Metallization, $MoX_a(L)_b$, selective deposition, ALD, semiconductor manufacturing

AF-MoP-27 Demonstration of ALD $Hf_xZr_{1-x}O_2$ Using Various Oxidant Sources Over Ultra-High Aspect-Ratio Structure for Memory Applications

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As memory devices continue to evolve toward higher density and enhanced performance, particularly in 3D architectures, the need for precise control over material properties at the nanoscale has become critical. $Hf_xZr_{1-x}O_2$ (HZO) is a promising material for next-generation memory applications, such as ferroelectric random-access memory (FeRAM) and high-k dielectrics for DRAM. Due to its ferroelectric properties and high dielectric constant, HZO plays a key role in improving device performance, lowering power consumption, and enhancing scalability. However, the successful integration of HZO into memory devices requires a precise, conformal deposition technique capable of maintaining uniformity across complex 3D structures.

In this work, we focus on demonstrating the deposition of HZO on ultra-high aspect-ratio structures using various oxidant sources, including anhydrous hydrogen peroxide (H_2O_2) and ozone (O_3) at 250°C. We will explore ALD process developments, such as stop valve processing and multiple dosing techniques, to successfully deposit HZO on features with aspect ratios as high as 10,000:1. The ultra-high aspect-ratio substrates used in this study feature advanced membrane technology that enables easier evaluation of HZO conformality across the complex structures without requiring complex sample preparation. In addition to optimizing the deposition process, material characterizations on blanket samples will be conducted to monitor the properties of the HZO films achieved using the developed ALD processes. Techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and other advanced characterization methods will be employed to assess film crystallinity, chemical composition, and other critical material properties. These analyses will ensure that the final HZO films meet the stringent requirements for next-generation memory applications, including high performance, scalability, and reliability for integration into advanced memory devices.

This work is supported by RASIRC. The BRUTE® Peroxide is provided by RASIRC Inc., and the ozone generator is provided by TMEIC. The authors would also like to express their gratitude to Chipmetrics for providing the ultra-high aspect-ratio substrates.

AF-MoP-28 Bottleneck-Effect on Thin-Film Conformality in High Aspect Ratio ALD

***Mikko Utriainen**, Jussi KInnunen, Jani Karttunen, Feng Gao,* Chipmetrics, Finland*; Anish Philip,* Aalto University, Finland

Atomic Layer Deposition (ALD) is an important method for conformal film deposition into high aspect ratio structures. It is widely used in advanced 3D semiconductor devices as well as batteries and MEMS devices. However, achieving an uniform film on thenarrow and complex shapes is challenging. Once 3D designs become more complex, or random shapes in porous structures increases, the small and variable opening dimensions will become more prevalent. These features will increase the difficulty of the deposition process development and optimization. The present understanding and research methodology to study the effects of narrow openings and bottlenecks is limited.

In this study, we demonstrate a novel experimental method to approach the problem. We used the PillarHall® lateral high-aspect ratio (LHAR) test structure to study the bottleneck effects on ALD thin film formation into the high aspect ratio cavities. The LHAR test structure setup enable to adjust the size of the entry into a cavity and study its effect on the film penetration profile. We performed thermal ALD to deposit Al_2O_3 on three LHAR structures and one vertical high aspect ratio (VHAR) structure. One LHAR sample, with a trench gap height of 500 nm, served as a reference with no bottleneck. In two other LHAR samples, we reduced the gap from 500 nm to 400 nm by adding a 50 nm layer at the trench opening, which created bottlenecks using non-conformal deposition of either Al_2O_3 or TiO_2. The VHAR structure had a bottleneck at the entry by design.

The measurements showed that without a bottleneck, the film could penetrate up to 152µm . When a bottleneck was present, the penetration depth decreased to 133–135µm, regardless of whether Al_2O_3 or TiO_2 was used. We employed line-scanning reflectometry to measure these structures, a method that could even differentiate between layers when TiO_2 formed the bottleneck. These results are in line with the diffusion-limited deposition model by Gordon et al. [1] and allowed us to compare the behavior of LHAR and VHAR structures. Based on our findings, carefully designed bottleneck structures could lead to improved models for predicting film growth in complex geometries, and this approach could be extended to cases with multiple bottlenecks within a cavity.

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AF-MoP-29 Low Temperature Deposition of SiO_2 and SiOC Films

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Atomic layer deposition (ALD) has emerged as a critical thin film deposition technique, particularly in the semiconductor, photonic, and energy storage industries, due to its ability to produce conformal, uniform films with atomic-scale precision. However, many ALD processes require elevated temperatures or harsh co-reactants to drive the reactions, which limits the applicability of ALD towards thermally or chemically sensitive substrates. This work presents the development and characterization of a novel low temperature ALD process for the deposition of silicon dioxide (SiO_2) thin films using a newly designed precursor and oxidant combination. The novel process enables the deposition of stoichiometric SiO_2 films at, near, or even below ambient temperatures and with acceptable cycle times, circumventing the need for high substrate temperatures and expanding the scope of SiO_2 ALD for temperature-sensitive applications. Furthermore, it will be shown that the highly specific and gentle oxidation conditions of the process afford ample opportunity opportunities for area-selective deposition, deposition of SiO_2 films on chemically sensitive organic substrates, or selective doping of the growing SiO_2 films with carbon-containing species for the formation of SiOC films. Plasma and thermal densification of the resulting films as well as characterization of the as-deposited and densified films will be discussed.

AF-MoP-30 Vanadium-Sulphide Layers with Atomic Layer Deposition

***Zsófia Baji**, Zsófia Bérces,* Centre for energy research, Hungary*; Zoltán Szabó, Zsolt Fogarassy, Péter Vancsó,* Centre for Energy Research, Hungary

Vanadium sulfides are a novel class of materials that have garnered significant interest due to their unique electronic, structural, and catalytic properties. Vanadium sulphide materials can exist in different compositions, among which VS_2 is the most researched as a 2D material. The other stoichiometries of vanadium sulfides have not received as much attention, and so far there is hardly any data on the structure and properties of VS. A comprehensive understanding of the full range of vanadium sulfides remains limited, prompting the need for advanced computational studies.

The present work compares the properties of atomic layer deposited VS layers from tetrakis(ethylmethylamino)vanadium (TEMAV) and H_2S, and computational models obtained with density functional theory (DFT) calculations. The ALD VS layers are amorphous, exhibiting a mixture of different stoichiometries with an internal composition of 63% V and 37% S. Upon removal from the ALD reactor, oxidation begins immediately. Annealing the samples in a sulfur-containing atmosphere promoted crystallization and resulted in a pure VS stoichiometry, with the top part of the layer polycrystalline and the lower portion remaining amorphous. The annealed VS layers were found to be semiconductors, with the sulfur treatment enhancing the stability and oxidation resistance of the material [1].

To further understand the grown material's properties, DFT calculations were performed. These simulations aimed to identify the different stable crystalline structures of VS that grown on the amorphous form of VS. Due to the very limited DFT data for VS, we employed different theoretical methods: standard DFT in the generalized-gradient approximation (GGA), GGA+U methods as a function of the U parameter, and hybrid functionals

(HSE) to reveal the electronic, magnetic and optical properties. Additionally, we investigated the effect of the defects to gain insights into its modified electronic behaviour and its potential applications.

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AF-MoP-31 Film and Surface Stress Measurements during Tungsten Atomic Layer Deposition*, **Ryan B. Vanfleet**, Steven M. George,* University of Colorado at Boulder

Film and surface stresses were measured during tungsten (W) atomic layer deposition (ALD) using *in situ* wafer curvature techniques. Tungsten was deposited at temperatures between 125 °C and 285 °C using tungsten hexafluoride (WF$_6$) and disilane (Si$_2$H$_6$) as the reactants on aluminum oxide (Al$_2$O$_3$) ALD surfaces. Tensile film stresses were observed at all deposition temperatures (Figure 1). The maximum film stress was ~2.2 GPa at 150 °C. The film stress decreased to ~1.0 GPa at 285 °C. For comparison, Al$_2$O$_3$ ALD films deposited at 125-285 °C have much smaller tensile film stresses of ~0.5-0.1 GPa. The large tensile stress in W ALD films may be generated at the grain boundaries. Atoms are too far apart at grain boundaries and experience an attractive force that wants to pull them together.

Surface stresses were also measured during the individual WF$_6$ and Si$_2$H$_6$ exposures during W ALD. For W ALD at 200 °C (Figure 2), the individual WF$_6$ exposures produced a tensile stress of ~+2 N/m. This tensile stress is correlated with the removal of sacrificial SiF$_x$H$_y$ surface species and the deposition of W and WF$_z$ surface species. The individual Si$_2$H$_6$ exposures then partially released the tensile stress with a compressive stress change of ~-1 N/m. There is a net tensile stress change per W ALD cycle of ~+1 N/m. The Si$_2$H$_6$ exposures redeposit sacrificial SiF$_x$H$_y$ surface species.

Other *in situ* stress measurements on SiO$_2$ native oxide on Si wafers have shown that the large tensile stresses in W ALD films can lead to delamination. The large tensile stresses in W ALD films can be reduced by periodic trimethylaluminum (TMA) exposures. The addition of TMA modifies the film surface and forces the re-nucleation of the W ALD film. The reduced stresses during the nucleation phase of W ALD growth contribute to a reduced tensile stress in the overall W ALD film. W ALD film stress can be tuned by the frequency of the TMA exposures.

AF-MoP-32 Modifying Vanadium Oxide by Atomic Layer Plasma Treatment*, **Ritwik Bhatia**, Mohammad Saghayezhian,* Veeco Instruments*; Ganesh Sundaram,* Veeco

VO2 shows a insulator to metal phase transition when it undergoes a transition in crystal structure from monoclinic to rutile as it is heated through the transition temperature ~ 68ºC. ALD VO2 deposited via alkylamido precursors (TDMAV and TEMAV) ~ 150-200ºC is amorphous as deposited and requires high temperature annealing (400-670ºC) to obtain a material with adequate crystallinity to show the metal-insulator transition [1,2,3].

ALD is a cyclic process with discrete steps – precursor introduction, precursor purge, co-reactant introduction, co-reactant purge. This allows the introduction of other steps into the ALD cycle to tune the film properties. One such approach (atomic layer annealing or atomic layer bombardment) injects energy to the film-growth surface by introducing an inert gas plasma step into the ALD cycle. It has been shown to produce epitaxial AlN [4] and GaN [5] films at low temperatures and to improve density and electrical properties of HfO2 [6].

In this work, apply the principle of atomic layer annealing to VO2. We have characterized changes to the film properties as a function of plasma exposure. VO2 grown with water as a co-reactant responds very differently to plasma exposure compared to O3 as a co-reactant. ALA causes a large increase in film roughness (porosity?) and reduction in refractive index for the water based process. The ozone based process shows a slight increase roughness and the refractive index due to ALA. Grazing incidence x-ray diffraction and Raman spectroscopy do not show crystallization of the film due to ALA.

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AF-MoP-33 Prediction of Adsorption/Desorption Equilibrium Constants and Surface Reaction Rate Constants Using Neural Network Potentials for ALD Process Design*, **Noboru Sato**, Naoki Tamaoki, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

For systematic design of ALD processes, adsorption/desorption equilibrium constants of precursors and reactive gases as well as surface reaction rate constants are required. Density functional theory (DFT) calculations can be used to determine the structures and energies of the adsorption states of chemical species and the transition states of surface reactions. However, the calculation of the reference vibrational frequencies needed for entropy and partition function evaluations requires an enormous computational cost. Consequently, discussions have often been based solely on changes in energy while neglecting entropy and partition functions. As a result, even when the activation energy for the surface reaction rate constant is obtained, it has been necessary either to assume a frequency factor of 10^{13} s^{-1} for the rate constant or to adjust the frequency factor to match experimental results.

Recently, atomistic simulation using neural network potentials (NNP) have attracted attention. An NNP is an atomic potential constructed by machine-learning on DFT calculation data, and it can perform calculations in less than one second that would otherwise take several hours using DFT. Therefore, atomistic simulators employing an NNP now enable the computation of reference vibrational frequencies within a practical time frame. In this study, we investigated whether atomistic simulator (Matlantis™) using the Preferred Potential (PFP) can be applied to the design of ALD process by calculating surface adsorption/desorption equilibrium constants and surface reaction rate constants with sufficient accuracy.

Figure 1 shows the results of calculating the transition state for the reaction in which CO$_2$ from the gas phase directly collides with an H atom adsorbed on Cu(111) to form a formate group, along with the vibrational frequencies of each mode in the transition state. The activation energy from the physisorption state is 80 kJ/mol; however, since an Eley–Rideal (E–R) type reaction is assumed, ΔE_{TST} becomes 53 kJ/mol after subtracting 27 kJ/mol corresponding to the physisorption energy. The presence of exactly one imaginary vibrational mode confirms that the structure is indeed a transition state. Based on these results, the reaction probability was calculated, and the comparison with experimental values [1] is shown in Figure 2. The reaction probability could be reproduced with an error of less than a factor of two. This indicates that the use of an NNP enables optimal design of the ALD process based on surface reaction rate constants.

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AF-MoP-34 *In Situ* Synchrotron Hard X-Ray Scattering Studies of the Structural Evolution of InAlN During Growth by PEALD*, **Jeffrey Woodward**,* U.S. Naval Research Laboratory*; Kenneth Evans-Lutterodt,* Brookhaven National Laboratory*; David Boris, Michael Johnson,* U.S. Naval Research Laboratory*; Zachary Robinson,* University of Rochester Laboratory For Laser Energetics*; Ruipeng Li, Masafumi Fukuto,* Brookhaven National Laboratory*; Karl Ludwig,* Boston University*; Charles Eddy, Scott Walton,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) is a promising technique for the growth of indium aluminum nitride (InAlN) and other alloys due to its atomic-level control of layer thicknesses and non-equilibrium process conditions, which can enable compositions within miscibility gaps. However, unlike the conventional model of atomic layer deposition (ALD) which assumes ideal layer-by-layer growth, the PEALD growth of highly crystalline films is often far more complex, with dynamic evolution of the nanoscale morphology occurring rapidly during the early stages of growth and depending on factors such as the plasma properties[1] and the strain evolution within the film.[2] Furthermore, compared to the growth of binary compounds, the growth of ternary alloys using the standard supercycle approach poses additional challenges as the constituent layers may exhibit differences in growth mode (e.g., island versus layer-by-layer) which could lead to deviations from the intended alloy composition, reductions in material quality, or even promote kinetic phase separation. Understanding how the process parameters and related properties influence the growth kinetics and the resultant material properties is essential for the realization of the PEALD growth of high quality alloy films. Grazing incidence small-angle x-ray scattering (GISAXS) using synchrotron radiation is well suited to this task, as it is nominally nondestructive, capable of probing nanoscale structure in real time, and is compatible with arbitrary process environments.

In this work, we investigate the influence of supercycle period on the nanoscale structural evolution of InAlN during growth by PEALD on gallium nitride (GaN) using *in situ* GISAXS experiments conducted at the Integrated *In Situ* and Resonant Hard X-ray Studies (ISR) beamline of National Synchrotron Lightsource II (NSLS-II). As the supercycle period is varied, significant differences in the evolution of the film structure are observed which do not follow a simple monotonic trend. The InAlN films are characterized *ex situ* using grazing incidence wide-angle x-ray scattering (GIWAXS), x-ray diffraction (XRD), in-plane grazing incidence diffraction (IP-GID), x-ray reflectivity (XRR), and atomic force microscopy (AFM).

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AF-MoP-35 Thermal ALD Vanadium Nitride (VN) as Next-Generation Electrode, ***Antony Jan**, Hae Young Kim,* Eugenus, Inc.

As semiconductor devices continue to shrink in scale, there is an increasing demand for electrode materials with improved properties. A current electrode material in use for many applications is titanium nitride (TiN), valued for its low resistivity, thermal and chemical stability, and compatibility with semiconductor processes. However, next-generation electrode materials--such as for DRAM applications--require lower resistivity, higher work function, higher density, and capability of highly conformal deposition into high aspect ratio structures. Vanadium nitride (VN) is one material that may possess these superior properties.

In this work, we have developed a thermal ALD vanadium nitride process on our 300 mm wafer tool. VN could be deposited over the tested range of 300 to 550°C, with a with-in-wafer thickness non-uniformity as low as 1%. On blanket wafers, VN films exhibited lower resistivity than reference TiN at all tested temperatures and thicknesses, as low as 110 μΩ*cm at a thickness of 10 nm. Work functions of VN films were consistently higher than for reference TiN, as measured by ultraviolet photoelectron spectroscopy (UPS). VN composition was roughly 1:1, with less than 1% of C or Cl detected by XPS. Grazing incidence x-ray diffraction (GIXRD) showed the films have a cubic structure with lattice parameter 4.11Å. VN films were highly conformal and could be deposited with step coverage values of 90 to 100%, into vias with aspect ratio as high as 70:1.

AF-MoP-36 ALD Synthesis of Transition Metal Phosphides, ***Raul Zazpe**, Jaroslav Charvot, Jhonatan Rodriguez-Pereira, Milan Klikar, Filip Bures, Jan Macak,* University of Pardubice, Czechia

The ever-increasing global energy demand together with the environmental issue originated from the use of fossil fuel, has triggered an intense search for sustainable and clean energy alternatives, such us hydrogen energy, biomass and solar energy among others. In this context, a pivotal key to deliver sustainable and superior energy systems lies on the rational design and development of high-quality and cost-effective catalyst offering enhanced stability, activity and selectivity. Consequently, intense efforts have been devoted in the search and synthesis of new catalyst materials to replace the scarce and expensive traditional noble metals (e.g. Pt, Pd, Au and Ru) for energy conversion and energy storage applications.

Among the recently explored novel catalyst materials, metal phosphides (MPs) have emerged in recent years, attracting significant attention thanks to their intriguing properties [1]. In particular transition metal phosphides (TMPs) exhibit striking properties. The moderately strong M−P bonds lend outstanding mechanical properties, high thermal stability and outstanding chemical resistance to chemical attack and oxidation in acidic and alkaline solutions. Additionally, Co, Ni, Mo-based phosphides demonstrated excellent catalytic and bifunctional properties, in particular towards water splitting as both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [2,3].

Herein, we present the synthesis of TMPs by thermal Atomic Layer Deposition (ALD) based on the use of different transition metal precursors and tris(trimethylsilyl)phosphine. The physical and chemical properties of the resulting TMPs thin films were extensively characterized by different methods, including atomic force microscopy, X-ray photoelectron spectroscopy and X-Ray diffraction. The presentation will introduce and describe the synthesis of the TMPs and the corresponding physical and electrochemical characterization toward electrocatalytic application.

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AF-MoP-37 Atomic Layer Deposition of a Low Carbon Hafnium Oxide Using (2-methylindenyl)tris(dimethylamido)hafnium and Ozone, ***Drew Hood**, Rong Zhao,* Entegris

High-K metal oxide layers, such as hafnium oxide, find applications across various device architectures ranging from the well established to the cutting edge .[1,2] Emerging applications, such as ferroelectrics for ultralow-power logic, continue to drive the development of hafnium oxide deposition.[3] In established and emerging applications new hafnium oxide precursors that can provide better uniformity, higher film quality, or reduce tool time are desirable.

Here we report a new hafnium oxide ALD precursor, (2-methylindenyl)tris(dimethylamido)hafnium (2-MeIndHf(NMe2)3), focusing on deposition performance using ozone and water. The results are compared to benchmark compounds tetrakis(ethylmethylamino)hafnium (TEMAHf) and tris(dimethylamido)cyclopentadienylhafnium ($CpHf(NMe_2)_3$) with a focus on growth per cycle (GPC), saturation, and film quality. Using process conditions optimized for each precursor, $2\text{-MeIndHf}(NMe_2)_3$ had the highest GPC at 0.86 Å/cycle, the lowest carbon incorporation, and better precursor/oxidizer saturation than benchmark compounds. Other advantages such as synthesis scalability are also discussed.

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AF-MoP-38 Rapid Low-Temperature Atomic Layer Deposition of HfO_2, *Xianhu Liang, Volkmar Hock, Hartmut Buhmann, **Johannes Kleinlein**, Laurens W. Molenkamp,* University of Wuerzburg, Germany

Hafnium oxide (HfO_2) thin films are extensively used as gate dielectrics. These films can be deposited by low-temperature atomic layer deposition using tetrakis-dimethylamido hafnium and water as precursor and oxidant, respectively, making them compatible with temperature-sensitive substrates. Recently, utilizing a homemade reactor, we successfully implemented such HfO_2 layers as gate dielectrics in various devices of thermally sensitive mercury telluride heterostructures [1-5]. However, in comparison to conventional (high-temperature) HfO_2 deposition protocols, at deposition temperatures of 30 °C, processes are time-consuming due to the long purge times involved [6]. In this talk, we present an innovative strategy to reduce the overall process time for a typical HfO_2 layer of 15 nm thickness by an order of magnitude, from 10 hours to 1 hour. This strategy involves reducing the purge time after each water pulse, accomplished by controlling the number of water molecules entering the reactor per pulse. This is achieved by significantly reducing the water vapor pressure in the source by cooling it below its freezing temperature, thereby forming water ice. The purge times are then adjusted to a minimum required for stable and reproducible deposition conditions. We present details of this process development and discuss the observed growth rate characteristics on thermally oxidized silicon wafers. For the optimized process parameters, the HfO_2 film thickness varies linearly with the number of cycles, and the deposition is homogeneous across the surface of the 2" sample stage. To demonstrate the applicability of this process, we apply the HfO_2 films as gate dielectric in lithographically patterned, high electron mobility quantum well devices. By performing electrical transport measurements, we investigate the gate performance at 1.4 K and find that the gate structures employing HfO_2 deposited using rapid low-temperature atomic layer deposition provide reliable and efficient gating, comparable to our previous technology. The relative permittivity of the HfO_2 extracted from the transport experiments is 11+-1 and the gate action is $1E12/Vcm^2$ for a 15 nm HfO_2 film. Consequently, we have established a rapid low-temperature atomic layer deposition process suitable for temperature-sensitive substrates that offers an order of magnitude reduction in deposition time.

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AF-MoP-39 Innovative Advanced Deposition Material (ADM) Technique for Low-Resistivity, High-Conformality Metal and Barrier Thin Films*, **Kok Chew Tan**, Changbong Yeon, Deok Hyun Cho, Jung Hun Lim, Jaesun Jung,* Soulbrain, Republic of Korea

As semiconductor device scaling approaches atomic dimensions, adopting next-generation metals for NAND, DRAM, and logic/foundry applications becomes crucial. Traditional metallization materials like copper and tungsten face increasing resistivity at reduced dimensions as well as challenges in barrier/liner scaling and deposition for complex patterns. Additionally, integrating high-performance metal gate electrodes with gate dielectrics layer requires addressing stringent electrical, thermal, and structural compatibility.

Molybdenum, with its low resistivity, short mean free path, and minimal diffusivity, offers a promising alternative for interconnects. For gate stacks integration, titanium nitride (TiN) serves as an effective barrier metal due to its high thermal stability, excellent diffusion resistance, and compatible work function. However, achieving uniform, ultra-thin, and defect-free TiN films with high conformality in high aspect ratio patterns is a significant challenge.

In this work, we present a novel Advanced Deposition Material (ADM) technique designed to deposit low-resistivity interconnect metals and barrier metal thin films including TiN at high temperatures with excellent step coverage. By leveraging inhibition and/or activation within each atomic layer deposition (ALD) cycle, the ADM method achieves precise control over film properties, resulting in low resistivity, enhanced conformality, and improved diffusion barrier performance. This ADM technique paves the way for advanced semiconductor device fabrication.

AF-MoP-40 Evaluation of a Hafnium Precursor with Higher Thermal Stability for the Atomic Layer Deposition of Hafnium Oxide Films*, Randall Higuchi, Khang Ngo, **Bhushan Zope**,* Merck KGaA, Darmstadt*; Joo-Yong Kim, Dong-Geun Lee,* Merck KGaA, Darmstadt, Republic of Korea

Hafnium oxide (HfO_2) is a critical material in the semiconductor industry used in DRAM, 3D-NAND and Logic Devices due to its excellent dielectric properties including a high dielectric constant and ferroelectric behavior (1). HfO2 films are used as high-k dielectric in capacitor for DRAM devices and in HKMG for Logic & DRAM devices. Additionally, these films are expected to find additional applications as blocking oxide in 3D-NAND and as BEOL capacitor dielectric in Logic devices. The key requirements of Hf precursors includes high thermal stability, enabling higher temp ALD window and HfO2 films with low film impurities and achieving excellent step coverage.

For this study we use the Chipmetrics Pillar Hall test vehicle to investigate the step coverage performance of this Hafnium precursor compared to other Hafnium precursors. By fixing the precursor flux during the dose and other process conditions, step coverage in the Pillar Hall trench can be compared at high aspect ratios.

In this study, we evaluate a Hf precursor that demonstrates superior thermal stability and improved step coverage up to 400°C compared to conventional precursors. This precursor has good vapor pressure for delivery for an ALD process and can be deposited up to 400°C without decomposition. The higher deposition temperature enabled HfO_2 growth with lower Carbon and Hydrogen content. Step coverage performance was evaluated and showed improved step coverage at 400°C compared to conventional precursors at their standard deposition temperature. The findings demonstrate the higher thermal stability and step coverage for this Hf precursor.

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AF-MoP-41 Modulation of $Hf_xZr_{1-x}O_2$ Thin Film Characteristics via ALD and ALE*, **Ming-Kuan Fan**,* National Tsing Hua University, Taiwan ; Taiwan Instrument Research Institute, Taiwan*; Yi-Cheng Chen,* National Tsing Hua University, Taiwan*; Chien-Wei Chen, Yang-Yu Jhang, Sheng-De Wong,* Taiwan Instrument Research Institute, Taiwan*; Hong-Luen Lin,* Tokyo Electron Taiwan Limited, Taiwan*; Ying-Hao Chu,* National Tsing Hua University, Taiwan

With the advance of the semiconductor industry, the pursuit of smaller transistor sizes presents a significant challenge in effectively controlling gate voltage. This challenge becomes particularly pronounced as transistors scale down, making it increasingly difficult to retain precise control over their on/off states. Herein, hafnium zirconium oxide ($Hf_xZr_{1-x}O_2$, HZO) has emerged as a significant material in the realm of higher-k. This solid-solution ceramic combines the advantageous characteristics of hafnium oxide (HfO_2) and zirconium oxide (ZrO_2), which is regarded as a promising candidate material for memory devices and related electronic devices. During the growth of nanolaminate HZO films, the TEMAHf and TEMAZr precursors were pulsed into the reaction chamber at different cycle ratios to form varied compositions. We used XPS survey spectra to quantify HZO stoichiometry precisely. This method can precisely control the atomic ratio of Hf and Zr to change the interface polarization state. With this modulation, the dielectric constant of HZO can be enhanced to 38, with equivalent oxide thickness below 0.6nm while maintaining a leakage current below $10^{-7}A/cm^2$.Besides, atomic layer etching (ALE) has been proposed for introduction into advanced semiconductor processes, especially in gate-all-around (GAA) or nano-sheet FET structures, due to its precise control and high etching selectivity. The crystallization temperature typically increases as the film thickness decreases due to the lower surface-to-volume ratio of thicker films favoring their crystalline phases. Consequently, when there are temperature constraints, amorphous HZO films may have to be grown thicker, annealed to crystallize, and then etched back to obtain the desired ultrathin crystalline thickness. In this study, we propose plasma ALE verification of $Hf_xZr_{1-x}O_2$ thin films using remote tetrafluoromethane (CF_4) plasma to achieve HZO surface fluorination and using dimethylaluminum chloride (DMAC) employed as the metal precursor for ligand exchange of fluoride removal layer. In the etching curve of HZO ALE, it can be estimated that the etching per cycle (EPC) of HZO at 400°C is approximately 0.55 Å/cycle.

AF-MoP-42 Atomic Layer Deposition of Lanthanum Oxide Using New La Precursors*, Junhyun Song, **Seungmin Han**, Jungwon Hwang,* Air Liquide, Republic of Korea

The continuous scaling of memory devices has led to challenges such as reliability issues due to leakage current and high power consumption. Lanthanum oxide (La_2O_3) is emerging as material for advanced memory devices because of its superior properties. For example, La_2O_3 is considered one of the promising materials for gate dielectrics due to its high dielectric constant (~27), wide bandgap (5.8~6.0eV), and thermodynamic stability in direct contact with Si. In addition, La_2O_3 is used as a dipole layer to adjust the effective work function of high-k metal gates, thereby reducing the threshold voltage. [1], [2]

Atomic layer deposition (ALD) is one of the most practical tools for advanced gate dielectric formation due to its precise thickness control, high uniformity and conformality. Air Liquide has developed three La precursors (La1, La2 and La3). Among them, La1 exhibits promising physical properties, including high vapor pressure and excellent thermal stability, making it a promising candidate for the ALD process. ALD evaluation was performed using La1 and ozone as the co-reactant. ALD window was observed up to approximately 350 °C, with a GPC >1A/cycle. Additionally, good step coverage (>90%) was achieved at 180 °C (S/C >90%, A/R=1:25). Carbon content within the films was dramatically reduced through a post-annealing process in the Ar atmosphere at 550 °C for 10 minutes.

Fig 1. Step coverage by using La1 with O_3 at 180°C

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AF-MoP-43 Ozone-Based Atomic Layer Deposition of Indium Oxide Thin Films: Impact on the Growth Rate and Its Uniformity of N_2 Supply in Ozone Generation

***Seung-Youl Kang**, Jaehyun Moon,* Electronics and Telecommunication Research Institute (ETRI), Republic of Korea*; Changbong Yeon, Jaesun Jung,* Soulbrain Co., Ltd., Republic of Korea*; Jong-Heon Yang, Chi-Sun Hwang, Seong-Mok Cho, Yong Hae Kim, Jae-Eun Pi, Seong-Deok Ahn,* Electronics and Telecommunication Research Institute (ETRI), Republic of Korea

Recently, thin indium oxide with a thickness of less than 5 nm has gained significant attention as an active material for thin film transistors due to its much higher electron mobility compared to other oxide semiconductors. When combined with the atomic layer deposition (ALD) method, it holds promise for use in back-end-of-line (BEOL) compatible transistors for monolithic 3D integration, as well as displays. The ALD method is particularly appealing for depositing ultrathin oxide semiconductors because it offers excellent thickness uniformity and controllability, with exceptional conformality that supports applications in monolithic 3D integration. To deposit oxide semiconductors using ALD, two key components are required: a metal precursor and a reactant. While various organometallic precursors for oxides have been developed and tested, the range of oxidants available is limited. Only a few molecules have been used as reactants, including water, hydrogen peroxide, ozone, oxygen plasma, and certain types of alcohols. However, not all oxidants are compatible with every precursor. For example, both water and ozone can be used with trimethylaluminum for Al_2O_3, whereas ozone is the only oxidant that can be used with trimethylgallium for Ga_2O_3, and DADI, InCp for In_2O_3. Ozone is often preferred for mass production because it is more reactive and easier to purge from the reaction chamber than water, though it does have drawbacks regarding deposition uniformity. In a previous report, we described the performance of TFTs using a new indium liquid precursor, DBADMI (N,N'-di-tert-butylacetimidamido)dimethylindium), renowned for its exceptional thermal stability across a wide temperature range (200°C to 350°C, which is the maximum temperature of our ALD equipment) . Like other indium precursors, DBADMI can be used to deposit In_2O_3 thin films with ozone, while water do not yield thin film formation. At an elevated temperature of 350°C, indium oxide films can be deposited with an acceptable growth per cycle (GPC) of approximately 1.1 Å per cycle, but the film thickness uniformity across the substrate was observed to be rather poor. In this article, we investigated the uniformity and growth rate of In_2O_3 thin films using DBADMI and ozone. Our findings revealed that the ratio of nitrogen (N_2) to oxygen (O_2) supply in the ozone generation process significantly affects the uniformity and growth rate of the In_2O_3 films. (Fig. 1.)

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AF-MoP-44 Promising ALD Precursor for Next-Generation Circuit Material: A Novel Ru-Based ALD Precursor with Lower Vaporization Temperature

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As the technology trend is focused on downscaling the size of transistors, the critical dimensions (CD) of integrated circuits (ICs) continue to shrink. Cu (copper) has the lowest bulk resistivity among other metals and therefore has become the primary material to use as a wire for electrical conductivity. However, as dimensions are scaled down, the resistivity of Cu increased by 2.5-fold under the size of 22 nm nodes, compared to bulk Cu. With the technology trend focused on downscaling the size of transistors, this phenomenon becomes fatal and will impact the overall performance of the circuit. According to past research, Ru (ruthenium) has a lower resistivity than Cu at thin metal lines starting from 10 nm in thickness. Therefore, it is expected to play an important role as a gate metal for next-generation circuit materials as an alternative to Cu.

Researchers can fabricate Ru metal thin films using various deposition techniques, such as electroplating, chemical vapor deposition, and atomic layer deposition (ALD). Among these methods, the ALD process has an extremely high application value because of its excellent film growth thickness controllability, step coverage, and large-area uniformity.

A high-quality ALD precursor needs to match several requirements, such as having a high vaporization rate, high reactivity, and high thermal stability. In this study, we successfully synthesized a novel ruthenium (Ru) ALD precursor, after TGA and DSC tests, it was found that the boiling point and vaporization temperature of this compound are lower than other commercial ruthenium precursors. Therefore, this precursor can be used at a lower processing temperature, which reduces energy costs and allows it to be applied to a wider range of ALD instruments with different specifications. At the same time, we are also developing other Ru precursors with different substituted groups to achieve different properties. We look forward to further developments of these precursors that can be used for next-generation circuit material.

AF-MoP-45 Low-Temperature ALD of Silicon Nitride Films Using Dis and Tis Precursors: A Strategy for Substrate Protection and High-Density Films

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Recently, various types of memory are being actively researched and developed to meet market demands for high performance and low power consumption. In emerging memory technologies, significant changes in cell materials and structures have made the gate spacer film increasingly important for protecting the cell material. Silicon nitride film has been used as gate spacer due to high density and reliable properties. ALD at high temperatures (>700℃) using DCS (Dichlorosilane, SiH_2Cl_2) has been the conventional method for deposition. However, this method can cause damage to the cell material, necessitating the development of alternative approaches to minimize such damage[1]. We investigated ALD process with DIS(SiH2I2) and TIS(SiHI3) in lower temperature(<300℃) to prevent the damage by chlorine and high temperature. We first examined the ALD window of DIS, focusing on process temperature and plasma power. Our results show that higher temperatures lead to lower impurity levels, resulting in a Si/N ratio close to 75% at 300°C, which is ideal for SiNx films. Additionally, lower plasma power resulted in lower impurity levels, with a Si/N ratio stabilizing at 75% under 100W plasma power. When analyzing film roughness, lower plasma power also led to smoother films, which is beneficial for device performance. We then compared the activation energies of DIS and TIS, finding that TIS exhibited a lower activation energy than DIS. We also studied the effect of varying TIS ratios (0%, 1%, 4.4%) on film properties. The growth per cycle (GPC) and refractive index (R.I.) showed minimal changes with different TIS ratios, but the film density increased with higher TIS content, despite similar impurity levels. This increase in film density, coupled with the lower activation energy of TIS, suggests that TIS-added films may provide enhanced SiNx gate spacer films that can effectively prevent initial damage and better protect the cell material during post-processing steps.

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AF-MoP-46 Thermal Atomic Layer Deposition of Silicon Carbonitride Using Carbon-Containing Silicon Precursor

***Okhyeon Kim**, Tanzia Chowdhury, Mi-Soo Kim, Changgyu Kim, Hye-Lee Kim, Jeong Woo Han, Jae-Seok An, Jung Woo Park, Won-Jun Lee,* Sejong University, Republic of Korea

Silicon carbonitride (SiCN) offers a lower dielectric constant and better etch selectivity than silicon nitride (SiN), making it a promising alternative to SiN for semiconductor device fabrication. It is particularly suitable as a low-k barrier in copper interconnects and as a gate sidewall spacer in memory devices. However, an optimal deposition method to ensure conformality in high-aspect-ratio structures has not yet been established. SiCN is typically deposited by plasma-enhanced chemical vapor deposition (PECVD) or plasma-enhanced atomic layer deposition (PEALD) [1], but these methods have conformality limitations. In this study, we present the thermal ALD of SiCN using carbon-containing silicon precursors at 600–800°C. The maximum ALD temperature was determined based on self-limiting behavior with increasing precursor and ammonia exposure and confirmed by step coverage analysis in high-aspect-ratio patterns. Films deposited at the maximum ALD temperature were characterized by X-ray photoelectron spectroscopy (XPS) analysis. Carbon atoms bonded to silicon were observed in the film at concentrations of approximately 10–30%, resulting in a low dielectric constant of 4.9. In addition, density functional theory (DFT) calculations explain the mechanism of carbon incorporation. The thermal ALD approach of this study enables the deposition of conformal films of ternary SiCN compositions without the need for complex supercycle ALD processes of SiN and silicon carbide (SiC).

AF-MoP-47 Atomic Layer Deposition of High-Quality SnO Thin Films Using Sn(EtCp)$_2$ Precursor*, **Fumikazu Mizutani**, Nobutaka Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; Tomomi Sawada,* National Institute for Materials Science,, Japan*; Toshihide Nabatame,* National Institute for Materials Science, Japan

Recently, SnO thin film has attracted attention because of an advantage of high hole mobility in the application of p-type oxide semiconductor. However, there are few reports of atomic layer deposition of conformal and defect-free SnO thin films.

Previously, we reported on ALD of SnO using a new Sn precursor (bis(ethylcyclopentadienyl) tin; Sn(EtCp)$_2$) [1]. Generally, ALD of SnO uses H_2O as a co-reactant for a divalent precursor, but no film growth was observed in ALD using Sn(EtCp)$_2$ and H_2O. To improve the adsorption of the precursor on the SnO surface, H_2O was used followed by H_2 plasma, which allowed the deposition of SnO thin films. However, when the elemental depth profile was analyzed, a small amount of Si was detected from the surface, indicating that a dense film had not been deposited.

To investigate the cause of this, the obtained SnO film was analyzed by XPS, and a small amount of Sn^0 signal was detected, indicating the presence of a metal component. This suggests that excessive reduction by the H_2 plasma occurred. In the previous report, SnO films were deposited on 150 mm Si wafers with native oxide films at a growth temperature of 200 °C, and saturation of reaction was confirmed with a H_2 plasma pulse time of 5 s. Therefore, this time we investigated whether it would be possible to deposit a dense film by shortening the H_2 plasma pulse time to 1 second.

FIG. 1 shows a comparison of film growth when the H_2 plasma time is 5 s and 1 s. As can be seen from FIG. 1, by shortening the H_2 plasma pulse time, the GPC became smaller, suggesting that the film became denser. The refractive index n at 380 nm of the SnO film deposited with 30 cycles, estimated by spectroscopic ellipsometry, was about 3.0 for both 5 s and 1 s H_2 plasma pulse times. However, for the film deposited with 100 cycles, the refractive index decreased to about 1.8 for the 5 s H_2 plasma pulse time, but only to about 2.6 for the 1 s H_2 plasma pulse time. This indicates that a dense film can be formed by shortening the H_2 plasma pulse time.

At the conference, we will report on the results of optimizing the H_2 plasma power and pulse time to deposit dense films and measure their electrical properties.

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AF-MoP-48 Damage-Free XPS Analysis of ALD HfO2, ZrO2 and HfZrOx Films Using Ar Cluster Ions*, **Seungwook Choi**, Ansoon Kim,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

HfO_2, ZrO_2, and their mixture, $Hf_xZr_{1-x}O_2$ (HZO), are high-k materials widely studied and applied in various aspects such as gate dielectrics, charge trapping layers, doped oxides, and the formation of nanolaminated layers with other high-k materials[1]. Recently, there has been active research in applications such as resistive RAM (RRAM) and ferroelectric RAM (FeRAM)[2,3]. To achieve optimal properties as gate oxides, HfO_2 and ZrO_2 are typically deposited using Atomic Layer Deposition (ALD). Ideally deposited, these oxides exhibit a high dielectric constant and low defect characteristics, resulting in low leakage current. A critical technique for determining the composition ratio and impurities of HfO_2, ZrO_2, and HZO to optimize ALD deposition conditions is X-ray Photoelectron Spectroscopy (XPS). XPS analyzes photoelectrons emitted from the sample surface upon exposure to X-rays, providing detailed information on the surface's chemical composition.To fabricate ALD thin films with optimal gate oxide performance, it is essential to conduct comprehensive analyses. Specifically, evaluating oxygen vacancies, impurity levels, and chemical composition is crucial, as these factors significantly influence the dielectric constant, leakage current, and stability of the gate oxide device. XPS provides precise and surface-sensitive chemical composition analysis, enabling detailed characterization of ALD thin films.However, ex-situ XPS measurements expose samples to atmospheric contaminants (CO_2, H_2O, etc.), which can hinder accurate chemical characterization of HfO_2, ZrO_2, and HZO films. While Ar+ ion beam sputtering is commonly used to remove surface contaminants, it can damage the film surfaces, leading to inaccurate analysis of oxygen defects and chemical composition of the films.In this study, surface chemical analysis of HfO_2, ZrO_2, and HZO thin films was performed using XPS after removing surface contaminants using monatomic Ar+ and Ar2500+ cluster ions. It was found that even at the lowest monoatomic Ar+ ion beam energy, all films were damaged, leading to reduced films (HfO_{2-x}, ZrO_{2-x}, HZO_2-x) due to preferential sputtering. In contrast, sputtering with Ar2500+ cluster ions effectively removed surface contaminants without causing damage, allowing accurate characterization of oxygen defects and chemical composition. Furthermore, XPS combined with Ar cluster ion beam analysis enabled successful carbon impurity analysis of films fabricated by both PE-ALD and thermal ALD without damaging the films.[1] W. Banerjee et al., *Small*, 2022, **18**, 2107575.[2] A. Chen, *Solid-State Electron*. 2016, **125**, 25.[3] M. Lanza et al., *Adv. Electron. Mater.* 2019, **5**, 1800143.

AF-MoP-49 Steric Hindrance of Hf Precursors and Film Growth of HfO2 Atomic Layer Deposition: Comparative Kinetic Monte Carlo Simulation*, **Yanwei Wen**, Haojie Li, Bin Shan, Rong Chen,* Huazhong University of Science and Technology, China

Hafnia (HfO2)-based ferroelectrics have attracted considerable attention for next-generation memory devices due to their robust ferroelectricity at ultra-thin scales. We combine density functional theory and kinetic Monte Carlo simulations to investigate the atomic layer deposition of HfO_2 films from TEMA–Hf and HfCp(NMe$_2$)$_3$ precursors using O_3 as the oxidant.Our results show that both precursors decompose preferentially at 2-coordinate O sites on the HfO_2 surface, while 3-coordinate O sites present much higher energy barriers. Kinetic Monte Carlosimulations reveal that growth-rates per cycle (GPCs) of TEMA-Hf and HfCp(NMe2)3 with O3 are 0.094~0.109 nm/cycle and 0.081~0.096 nm/cycle from 150°C to 350°C, aligning closelywith experiments. The slower GPC observed forHfCp(NMe$_2$)$_3$ is attributed to the greatersteric hindrance of cyclopentadienyl ligand(Cp)compared to the dimethylamide(NMe$_2$) groups.Film morphology analysissuggests TEMA-Hf leads to smoother HfO_2 films.Nitrogen incorporation remains at about 1% for TEMA–Hf and HfCp(NMe$_2$)$_3$, consistent with experimental observations,while the concentration of O vacancies slightly decreases with the increase of deposition temperature. These findings provide insight into how precursor selection and atomic-level reaction pathways influence film growth and composition, thereby affecting the ferroelectric performance in HfO_2-based devices.

AF-MoP-50 In-Situ Spectroscopic Ellipsometry for Transition Metal Oxide Growth Control in Remote Plasma ALD Processes*, Yousra Traouli, Ufuk Kilic,* University of Nebraska - Lincoln*; Mathias Schubert, **Eva Schubert**,* University of Nebraska-Lincoln, USA

In this work, we investigate the real-time growth dynamics for transition metal oxide ultra-thin films (ZnO, WO_3, TiO_2) using Plasma-Enhanced Atomic Layer Deposition (PE-ALD) and in-situ spectroscopic ellipsometry (SE). Our primary focus is on characterizing the nonlinear growth regime during the initial nucleation phase and its transition into a stable, self-limiting layer-by-layer growth. By leveraging in-situ SE, we track the cyclic surface modifications, monitoring the evolution of film thickness and surface roughness throughout the deposition process[1]. The ALD growth utilizes organometallic precursors for the transition metals, with remote oxygen plasma and a water step as co-reactants to optimize film quality and uniformity. Additionally, we analyze the temperature dependence of the growth behavior to gain deeper insights into nucleation dynamics and film evolution[2]. Post-deposition structural and chemical characterization including scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) complements our in-situ findings. This study provides a comprehensive understanding of ALD growth mechanisms for transition metal oxides and offers valuable guidelines for optimizing deposition parameters to achieve high-quality, precisely controlled thin films.

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AF-MoP-51 Plasma-Enhanced ALD Process for Boron Carbide Films: Towards Tunable B:C Ratio*, **Catherine Marichy**, Neil Richard Innis, Abdhulhamid Afolabi,* Universite Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100, France*; Olivier Boisron,* Universite Claude Bernard Lyon 1, CNRS, ILM, Villeurbanne, F-69100, France*; Didier Leonard,* Universite Claude Bernard Lyon 1, CNRS, ISA, Villeurbanne, F-69100, France*; Colin Bousige, Catherine Journet,* Universite Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100, France

Boron carbide (B_xC) is a well-known ceramic material with high chemical and thermal stability, super-hardness, and a large neutron absorption cross-section. It is used in various applications such as refractory and cutting tool ceramics and neutron absorbers and detectors. Less explored are its electronic and optoelectronic properties. B_xC is a rather unknown semiconductor with tunable band gap[1,2] as a function of its B:C stoichiometry. Investigating its semiconductor properties requires its deposition as thin films with precise control over thickness, structure and composition. While PVD[3,4] and especially CVD[4–9] have shown potential for fabricating boron carbide thin films, ALD for B_xC remains largely unexplored[10] despite its advantages in terms of thickness control, uniformity and conformality.

In this study, amorphous B_xC thin films with atomic-level thickness control are successfully deposited by PEALD from triethylboron (TEB) and H_2 plasma[11]. A tunable B:C ratio is achieved by adjusting the process parameters. While the deposition temperature does not significantly affect the stoichiometry, special attention is given to the effect of plasma parameters, such as plasma mode (direct vs remote), H_2 flux and plasma power on the film composition. Plasma species not only remove the ethyl groups from TEB, but can also decompose by-products that may lead to additional carbon introduction into the film. A possible surface etching effect must also be considered.

The developed PEALD process of B_xC is discussed with a focus on the evolution of the film composition as a function of the plasma parameters. The plasma composition is monitored by in-situ optical emission spectrometry. The films are characterized in terms of thickness, morphology, structure and composition using various characterization techniques: ellipsometry, SEM and TEM, AFM, XPS, and ToF-SIMS. Attention is also paid to the physicochemical properties of the layers obtained, including their band-gap.

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AF-MoP-52 A Theoretical Study on High-Temperature ALD of TiN Using CP(CH_3)$_5$Ti(Ome)3 as a Precursor*, **Jae Min Jang,*** Hongik University, Republic of Korea*; Hye Won Park,* Incheon National University, Republic of Korea*; Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; Han-Bo-Ram Lee,* Incheon National University, Republic of Korea*; Bonggeun Shong,* Hongik University, Republic of Korea

In the field of semiconductor technology, titanium nitride (TiN) plays a critical role as a versatile material, serving as either diffusion barrier, adhesion layer, and conductor. As semiconductor devices continue to miniaturize, there is a demand for deposition methods of ultra-thin, easy thickness control, improved uniformity, and conformality, such as atomic layer deposition (ALD). For the above-mentioned applications of TiN, high temperature for the deposition process is often desirable. The precursors for high-temperature ALD of TiN, chlorine-containing Ti precursors may cast concerns regarding contamination and unwanted etching, while other Ti precursors often pose limitations in process temperature due to lack of thermal stability. In this regard, development of new ALD chemistry suitable for high temperature process is desirable. In this work, surface chemistry of Cp(CH_3)$_5$Ti(OMe)$_3$ (trimethoxy(pentamethylcyclopentadienyl)titaniumor TMPMCT)as a precursor for high-temperature ALDof TiNis investigated. Machine learning interatomic potential (MLIP) calculations are applied to elucidate the surface reaction mechanisms of TMPMCT. At high temperatures, the TiN surface is expected to have low coverage of H-containing functional groups due to desorption of NH_3 or H_2 [1]. Therefore, dissociative adsorption pathways of TMPMCT on the pristine TiN surface without surface functional groups are considered. The reactions under NH_3 exposure for removal of the ligands remaining on the surface are also elucidated. The changes in the Gibbs energy as functions of temperature are calculated as measure of the spontaneity of the reactions. Current work elucidates the chemistry of a potential new ALD process via molecular level theoretical investigations.

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AF-MoP-53 Adsorption of Hf Ald Precursor on Pristine HfO₂ Surface Without Hydroxyl Groups*, **Woong Pyo Jeon**, Miso Kim, Jinwoo Lee, Bonggeun Shong,* Hongik University, Republic of Korea

Hafnium oxide (HfO_2) stands as a prominent high-k dielectric material extensively employed as the gate oxide of nano-scale MOS devices. Atomic layer deposition (ALD) is a viable solution for the deposition of ultra-thin HfO_2 films with precise thickness control, enhanced uniformity, and conformality. Various oxygen sources are used for HfO_2 ALD, among which ozone or oxygen plasma can generate films devoid of surface functional groups such as hydroxyls (OH). Still, ALD of HfO_2 can occur on these surfaces, which may involve adsorption of the ALD precursors through ligand decomposition or ligand-mediated reactions [1]. In this study, the adsorption mechanism of TDMAH (tetrakis(dimethylamido)hafnium) on surfaces of pristine monoclinic HfO_2 without OHtermination is studied utilizing machine-learned interatomic potential (MLIP) and density functional theory (DFT) calculations. Accounting for potential byproducts arising from TDMAH adsorption and subsequent ligand desorption, diverse reaction pathways are explored, obtaining adsorption and activation energies for each scenario. To guide future experimental studies, vibrational spectra of the potential product structures are also calculated. Current study shows that ALD of oxides can proceed even without OH functional groups.

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT, RS-2023-00210186).

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AF-MoP-54 Sequential Adsorption of Dimethyl Zinc and Trimethylaluminum and Its Application to Zinc Aluminum Oxide Atomic Layer Deposition*, Haruto Suzuki, Satoshi Suzaki, Hibiki Takeda, Ryo Miyazawa, Bashir Ahmmad, **Fumihiko Hirose**,* Yamagata University, Japan

Zinc aluminum oxide films are applicable as wide-gap oxide semiconductors and for anti corrosion although the dependence of electronic properties on the zinc to aluminum atomic ratio is still unknown. In our laboratory, we have developed room-temperature atomic layer deposition of complex oxide using sequential adsorption where the two metal precursors are introduced to the surface sequentially to produce the mixed precursor saturated surfaces. This is assumed to allow for formation of perfectly atom dissolved oxide. In this experiment, we used dimethyl zinc (DMZ) as a Zn precursor and trimethylaluminum (TMA) as an Al precursor. The oxidizer was plasma excited humidified argon. We examined DMZ first introduction, followed by TMA adsorption. The atomic content ratio of Al to Zn was controlled by the exposure of the second gas of TMA. By using in-situ observation of IR absorbance spectroscopy, the TMA adsorption was modeled with one- and two-site adsorption models. Here TMA was assumed to adsorb on the DMZ-adsorbed surface with one or two unoccupied OH sites. Based on the dependence of TMA coverage on the DMZ exposure, the atomic ratio of Al to Zn was predicted. The related experimental results are presented, and the surface reaction mechanism is discussed in the conference.

AF-MoP-55 A Study on Laterally Controlled Distribution of Elements in InZnO Thin Films by Atomic Layer Modulation

Dong-Hyun Lim, Ajou University, Republic of Korea*; Kyung-Won Park, Ji-Hye Choi,* ATIK CO., LTD., Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea

This study investigates the growth mechanisms and elemental distribution in InZnO (IZO) thin films using atomic layer modulation (ALM), a technique that enhances elemental distribution by sequentially introducing two precursors that react with a single counter reactant, thereby allowing for the formation of a monolayer multicomponent thin film. [1] A key finding is the conversion reaction where In metal transforms into Zn metal during the deposition process, as illustrated in Figure 1(a). The in-situ quadrupole mass spectrometry (QMS) analysis in Figure 1(b) confirms this reaction, showing that after feeding [3-(dimethylamino)propyl]dimethylindium (DADI) and pulsing diethylzinc (DEZ), In is converted into the ethyl ligand-bound $In(Et)_3$, indicating the formation of a zinc-rich film via ALM. Furthermore, the comparative analysis of homogeneous IZO films grown via ALM and laminate structures deposited by the supercycle method highlights the lack of research on how elemental distribution affects channel properties in oxide semiconductors. This comparison is expected to significantly contribute to the field of oxide semiconductor research. Lastly, it is noteworthy that ALM has primarily been studied for dielectric materials, with no prior investigations conducted on oxide semiconductors, marking a novel aspect of this research.

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AF-MoP-56 Comparative Study on the Impacts of Anhydrous and Hydrous H_2O_2 on ALD Hafnium Oxide Growth on Titanium Nitride Surface

Dan Le, RASIRC*; Jin-Hyun Kim, Thi Thu Huong Chu, Soubhik De, Dushyant Narayan, Minjong Lee,* University of Texas at Dallas*; Walter Hernandez, Josh Garretson, Adrian Alvarez, Jeffrey Spiegelman,* RASIRC*; Jiyoung Kim,* University of Texas at Dallas

HfO_2-based ferroelectrics have emerged as prominent materials for memory applications due to their unique electrical properties, even at the sub-nanometer scale. However, interface-related challenges, such as relaxation, imprint, fatigue, and breakdown, continue to pose significant concerns, especially for ferroelectric films thinner than 5 nm [1]. Previous studies have shown that the choice of oxidant sources during ALD HfO_2-based ferroelectrics plays a crucial role in oxide interface formation [2]. Therefore, selecting the appropriate oxygen source or developing effective interface engineering processes is essential to overcoming these interface-related challenges.

In our earlier studies, we observed that HfO_2-based ferroelectrics achieved using anhydrous H_2O_2 exhibited a higher growth rate and enhanced electrical properties [3]. However, our *in-situ* investigation of ALD HfO_2 on titanium nitride (TiN) substrate at 250 °C revealed that anhydrous H_2O_2 saturated the TiN surface with hydroperoxyl groups, leading to the formation of a limited interface, whereas H_2O formed little to no interface [2]. A key question remains whether a combination of H_2O and H_2O_2 may help reduce HfO_2–TiN interface formation while maintaining the enhanced properties of the HfO_2 layer. In this study, we focus on investigating the effects of hydrous H_2O_2 on interface formation and growth mechanism of ALD HfO_2 on TiN substrate. Using *in-situ* reflectance absorption infrared spectroscopy (RAIRS) and complementary analytical techniques, we aim to gain deeper insights into the underlying phenomena. Throughout the study, alongside TDMA-Hf as the metal precursor, the hydrous H_2O_2 (4:1 H_2O/H_2O_2 ratio) is delivered via a gas delivery system to ensure a stable and constant oxidant supply. While the IR results reveal some similarities, a distinct difference between anhydrous and hydrous H_2O_2 was observed, as the peak associated with hydroperoxyl groups was absent in the case of hydrous H_2O_2. The differences in the available surface species during the hydrous H_2O_2 pulse may influence the growth of HfO_2. In addition to IR analysis, the impacts of hydrous H_2O_2 on growth characteristics, and material properties, including chemical composition, density, ferroelectricity, etc. will also be carefully evaluated. Detailed experimental procedures and results will be presented.

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AF-MoP-57 Computation of Al_2O_3 ALD by Trimethylaluminum with Kinetic Monte Carlo and Neural Network Potential

Yichen Zou, *Yuxuan Wu,* The University of Tokyo, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic Layer Deposition (ALD) is widely utilized in semiconductor manufacturing owing to its method of alternately introducing a precursor and reaction gas, which relies on the surface saturation adsorption of the precursor. This approach ensures excellent uniformity in thickness and controls variations in processing conditions, but is challenged by its growth rate compared with other deposition methods. Investigation into the growth rate of ALD has drawn tremendous attention in the experiments but could be facilitated by emerging computation methods that cut the cost. Traditional computational methods, such as Density Functional Theory (DFT), offer insights into surface adsorption and reactions and are time-intensive when predicting the growth rate per cycle for ALD applications, particularly for large metalorganic compounds. To overcome these challenges, we are leveraging Kinetics Monte Carlo (KMC, an emerging time-scale reaction simulation method) and Matlantis™ (a cutting-edge atomic-level simulator that utilizes neural network potentials) to investigate the adsorption of Trimethylaluminum (TMA) during Al_2O_3 ALD using H_2O as the reactant.KMC is a numerical simulation method based on stochastic processes, which is mainly used to study the dynamic evolution of complex systems. KMC is not only concerned with the equilibrium properties of the system but also directly simulates the time-dependent kinetic behavior, which is suitable for the study of non-equilibrium processes with multiple possible events such as the ALD process. The powerful Matlantis™ calculates energies accurately and efficiently for multiple TMA molecules adsorption and reaction of multiple TMA molecules on the surface, and the energies are introduced into KMC to predict the growth rate of Al_2O_3 in each cycle. Both the KMC and Matlantis' calculations can be performed at extremely fast speeds, with time spent on a scale of minutes. In the following figures, we successfully predicted the adsorption kinetics of TMA during the TMA supply step, which showed a mass increase of 36 ng/cm^2 in approximately 0.3 seconds. Our TMA adsorption and growth simulations show strong agreement with previous DFT calculations and Quartz Crystal Microbalance (QCM) experimental results. In addition, our study revealed that some carbon remained inside the film. The KMC simulations were performed at different temperatures and water pulse times. The results show that both the temperature and water pulse time have important effects on the carbon residue in the film. Low temperature and short water pulse time significantly increased the carbon residue.

AF-MoP-58 Comparison of ALD SiN Film Properties Based on Synthesis Precursor, Process Temperature, and Conditions

Jaeyoung Lim, *Hanseong Kim, Sunki Min, Kang-sub Yim, Sun Jung Kim,* Samsung Electronics Semiconductor R&D center Semiconductor Processing Development, Republic of Korea

ALD SiN films play a crucial role in semiconductor processes, serving various applications. While different precursors are utilized for ALD SiN synthesis, the halogen-based precursor dichlorosilane (DCS) is widely adopted due to its cost-effectiveness and excellent film properties. However, its relatively low reactivity necessitates high-temperature plasma processing, posing limitations on film quality enhancement. In contrast, diIodosilane (DIS), another halogen-based precursor, exhibits higher reactivity, allowing for low-temperature plasma processing. This study compares the film characteristics of ALD SiN synthesized using DCS and DIS precursors under varying process temperatures and conditions. The findings aim to provide insights into optimizing ALD SiN synthesis methods for high-performance semiconductor logic devices.

ALD Fundamentals
Room Halla Hall AB - Session AF1-TuM
Mechanism and Theory I

Moderators: Christophe Vallée, University of Albany, **Charles H. Winter**, Wayne State University

8:00am **AF1-TuM-1 The Mechanism of Thermal ALD of Silicon Carbonitride from Chloroalkylsilanes and Ammonia – Theory Meets Experiment*, Simon Elliott,*** Schrödinger, Ireland*; Jiyeon Kim, Paul Lemaire, Dennis Hausmann,* Lam Research

Carbon-doping of silicon nitride or silicon oxide results in a lowering of the dielectric constant and etch rate. The C-doped derivatives are therefore being used to replace the parent films in many applications in FEOL semiconductor manufacturing, such as for spacers and gap fill. Traditionally these C-doped films are deposited by CVD methods, but recently ALD methods have been formulated using silicon precursors with Si-CHx bonds. Maintaining the Si-CHx bond has been challenging due to its propensity to cleave under plasma conditions or at high temperatures. For these reasons, precursors that can be used in a low temperature thermal ALD process are highly desired.In this work we investigate whether ammonia is viable as a thermal ALD co-reagent for this application and what mixture of chloro and alkyl ligands are most favorable in the silicon precursor.

We use density functional theory (DFT) to compute the atomic-scale structure of surface intermediates and the mechanism of potential ALD reactions and complement this with detailed characterization during substrate exposure experiments.

Looking first at the co-reagent, we investigate the kinetics of proton transfer from ammonia to a model silyl fragment on an aminated surface. Four proton transfer pathways are obtained for HCl elimination, all with high barriers (>1.2 eV) that are indicative of low Bronsted acidity and suggest that side-reactions will compete with the ALD process. Three pathways are obtained for CH4 elimination with even higher barriers (>2.5 eV). Therefore, up to moderate temperatures, terminal-CH3 is likely to survive ammonia treatment and be incorporated into the film, and this could be a route to C-doping. Residual gas analysis (RGA) and quartz crystal microbalance is used to monitor whether HCl or CH4 is in fact evolved during each half reaction.

The second part of the study looks at the effect of various combinations of chloro and methyl ligands in candidate Si precursors, both monomers (SiCl4, SiHCl3, SiCl3Me, SiH2Cl2, SiHCl2Me, SiCl2Me2) and dimers (Si2Cl6, Si2Cl4Me2). Structural models are generated efficiently of the >100 surface intermediates that can potentially occur through physisorption, chemisorption via ligand elimination and etching by exchange with surface amines. For each precursor, DFT-based thermodynamics reveal that the most favorable intermediate is surf-SiCl3 up to about 250C, surf-Cl2 up to 450C and surf-Cl at higher temperatures, with associated predictions of ALD growth rate. Film composition and growth rate is then validated experimentally by ellipsometry (SE) and infrared red spectroscopy (ATR-FTIR), ex-situ but with an inert atmosphere glove box.

8:15am **AF1-TuM-2 Mechanistic Studies on Area Selective ALD of Iridium*, Heta-Elisa Nieminen,*** *Matti Putkonen, Mikko Ritala,* University of Helsinki, Finland

The importance of self-aligned film deposition processes is obvious when considering the complexity of the devices being currently manufactured. Every process that can directly deposit only on selected areas may decrease the number of processing steps needed. When the growth is dictated by surface chemistry also issues related to pattern misalignment can be avoided. Finding new self-aligned thin film deposition processes becomes yet more important as the device dimensions are shrinking. Understanding the mechanism behind the selectivity helps in finding new process and surface combinations. In this work, the reason behind a selective growth of iridium on a set of substrates that are chemically alike is studied. The surface reactions and the selectivity mechanism are studied with ALD-UHV cluster tool by using *in vacuo* XPS, LEIS and TPD together with *in situ* QCM.

Excellent area selectivity in ALD of metallic iridium on a wide selection of substrates was initially found by Zhang et al. (*Chem. Mater.* 2022, 34, 8379-8388). The depositions were done with iridium(III) acetylacetonate, $Ir(acac)_3$, and O_2 as precursors. The growth is believed to start with a ligand exchange reaction between surface -OH group and the $Ir(acac)_3$ precursor. Initial hypothesis for the selective growth is that the weakly acidic byproduct formed in the ligand exchange reaction, Hacac, adsorbs preferably on more basic surfaces passivating them. In the current work, two surfaces on which iridium was deposited successfully, native SiO_2 terminated Si and *in situ* deposited Al_2O_3, are compared to two surfaces on which the deposition did not succeed, Al_2O_3 and HfO_2. The latter mentioned oxides as well as the native SiO_2 terminated Si were exposed to air and airborne hydrocarbons prior to the iridium deposition.

The passivation of the non-growth surfaces was clearly confirmed with the analysis methods used and details of the nature of the passivating compounds were resolved. Also, the possible role of the adventitious hydrocarbons in the beginning of the film growth was studied. The increased knowledge about the surface reactions can guide the thinking when selectivity is aimed on new process and surface combinations.

8:30am **AF1-TuM-3 ALD Outstanding Presentation Award Finalist: Like Boots or Hearts: The Kinetics of Precursor Decomposition*, Sean Barry,*** Carleton University, Canada

One of the main differences between Chemical Vapor Deposition (CVD) and atomic layer deposition (ALD) is gas-phase reactivity: we anticipate precursors to react together or independently in the gas phase in CVD but generally expect ALD precursors to arrive at the substrate intact. However, thermal activation of a precursor in the gas phase can benefit ALD saturation by producing a more active chemical species.

Our group often uses an *in-situ* solution-phase method to discover thermal behaviour and track the kinetics of decomposition. Samples are flame-sealed in a glass tube with an appropriate solvent and monitored by nuclear magnetic resonance (NMR) spectroscopy. This characterization method is common in synthetic chemistry and can be used to analyse a variety of nuclei independently, and this technique can commonly and easily assess protons. Using this technique in conjunction with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), we can build structure-function relationships to help design better precursors.

The framework $Mo(VI)(=N^tBu)_2Cl_2.(L\text{-}L)$ (where L-L is a chelating ligand) allows us to easily investigate the role of chelate ligands in precursor design due to the thermal stability of the imide/chloride core. This talk will center on measuring the thermodynamics of precursor thermolysis through Eyring analysis and detail the implications of β-H versus γ-H elimination, as well as differentiating *inter*-molecular vs. *intra*-molecular reactivity. The presentation will show detailed reaction coordinates and different mechanistic thermolysis pathways for a growing family of Mo(VI) compounds.

8:45am **AF1-TuM-4 Reaction Mechanism of Atomic Layer Deposition of Zirconium Oxide Using Tris(dimethylamino)cyclopentadienyl Zirconium*, Yong Richard Sriwijaya,*** *Hye-Lee Kim, Okhyeon Kim, Khabib Khumaini,* Sejong University, Republic of Korea*; Romel Hidayat,* PT PLN, Indonesia*; Won-Jun Lee,* Sejong University, Republic of Korea

A promising strategy for the development of advanced atomic layer deposition (ALD) precursors is the design of heteroleptic metal-organic compounds in which multiple ligand types are attached to a metal center. These heteroleptic precursors offer advantages over homoleptic counterparts, such as improved thermal stability while maintaining high reactivity. A notable example is tris(dimethylamino)cyclopentadienyl zirconium ($CpZr(NMe_2)_3$), which has successfully replaced the homoleptic precursor tetrakis(ethylmethylamino)zirconium ($Zr(NEtMe)_4$) in the fabrication of zirconium oxide (ZrO_2) films for dynamic random-access memory (DRAM) devices. Compared to Zr(NEtMe)4, CpZr(NMe2)3 exhibits better thermal stability, enabling better conformality at high process temperatures of 300°C with a growth per cycle of ~0.9 Å [1]. However, the competition between the NMe_2 and Cp ligands during surface reactions complicates the identification of the final chemisorbed species, which is important for designing the precursor for high-temperature ALD. In this study, we investigated the reaction mechanism of ZrO_2 ALD using a combined approach of *ab initio* calculations and *in situ* characterization. Density functional theory (DFT) calculations were performed to model the stepwise surface reactions of $CpZr(NMe_2)_3$ on a ZrO_2 surface, while *in situ* quartz crystal microbalance (QCM) analysis was used to study the ALD process with alternating precursor and ozone (O_3) exposures. DFT results indicate that the first two NMe_2 ligands are readily released during chemisorption of the Zr precursor with low activation energies of 0.22 eV and 0.16 eV. In contrast, the release of the Cp ligand or the third NMe_2 ligand is thermodynamically unfavorable due to its endothermic nature and high activation energy. As a result, the final chemisorbed surface species is predicted to be $O_2ZrCp(NMe_2)$*. QCM analysis confirms the release of two

NMe_2 ligands during the first ALD half-cycle, which agrees with the DFT results. This study demonstrates the effectiveness of integrating DFT calculations with QCM analysis to gain mechanistic insight into ALD reactions, especially when heteroleptic precursors are involved.

References [1] J. Niinisto et al., J. Mater. Chem. 18, 5243 (2008).

9:00am **AF1-TuM-5 A Study on the Correlation of Surface Chemistry to Electrical Properties of Ultra-thin Oxide Semiconductors by Atomic Layer Deposition: A Case Study of Indium Oxides Thin Films*, Joohyeon Lee,*** Ajou University, Republic of Korea*; Dohee Kim, Ja Yong Kim, Jong Young Lee, Seung Wook Ryu,* SK Hynix, Korea*; Il Kwon Oh,* Ajou University, Republic of Korea

Atomic layer deposition (ALD)-grown ultra-thin In_2O_3 offers promising solutions with amorphous films at sub-3 nm thicknesses, allowing effective tuning of mobility and V_{th} based on thickness [1].

Materials and electrical properties of ultra-thin ALD films are significantly dependent on surface chemistry. For example, $HfCl_4$, with simple chlorine ligands, achieves a higher growth per cycle (~1.3 Å/cycle), lower interface trap density (1.86×10^{11} eV^{-1} cm^{-2}), and reduced leakage current density (3.94×10^{-7} A/cm^2 at $V_{FB} = -1V$). This is due to efficient oxidation and minimal steric hindrance, resulting in stoichiometric films with fewer oxygen vacancies. In contrast, $Hf(N(CH_3)_2)_4$, with bulky dimethylamino ligands, exhibits slightly lower GPC (~1.2 Å/cycle) and higher oxygen vacancy concentrations, leading to increased D_{it} (8.96×10^{11} eV^{-1} cm^{-2}) and leakage current (2.25×10^{-6} A/cm^2). Steric hindrance limits oxidant access, resulting in sub-stoichiometric HfO_{2-x} phases [2]. This highlights the critical role of ligand structure in determining film stoichiometry, defect density, and electrical performance, emphasizing the need for a comparative study for ultra-thin film formation using ALD.

In this study, we investigate the reaction mechanisms and surface chemistry of two indium precursors, [3-(dimethylamino)propyl]dimethyl indium (DADI) and trimethyl indium (TMI), for ALD-grown ultra-thin In_2O_3 films using O_3 as the reactant. DADI, containing dimethylamino and methyl groups, introduces greater steric hindrance compared to TMI, which has only methyl groups. This difference affects adsorption density, oxidizer accessibility, and oxygen deficiency during film growth, leading to variations in film composition, density, and electrical properties. To evaluate these differences, quadrupole mass spectrometry (QMS) will analyze ALD byproducts, X-ray photoelectron spectroscopy (XPS) will assess impurity levels and oxygen vacancies, and transmission electron microscopy (TEM) will confirm film uniformity. Physical properties such as morphology and density will be analyzed using atomic force microscopy (AFM) and X-ray reflectometry (XRR). Finally, a bottom-gate TFT will be fabricated to correlate these properties with electrical performance, providing a comparative evaluation of the precursors for BEOL integration into monolithic 3D devices.

References [1] Si et al., Nano Lett., 21, 1, 500–506 (2021) [2] Oh et al, J. Mater. Chem. C 6, 7367 (2018).

9:15am **AF1-TuM-6 Catalytic Role of Silane(SiH4) in Enhancing Titanium Nitride(TiN) Atomic Layer Deposition(ALD)*, Hu Li,*** Tokyo Electron America Inc.*; Taichi Monden, Masaaki Matsukuma,* Tokyo Electron Technology Solutions Ltd., Japan*; Jianping Zhao,* Tokyo Electron America Inc.*; Yoshitada Morikawa,* Osaka University, Japan*; Peter Ventzek,* Tokyo Electron America Inc.

Titanium nitride (TiN) films are crucial for microelectronics applications due to their exceptional electrical conductivity, thermal stability, and barrier properties. Atomic layer deposition (ALD) has emerged as a preferred method for TiN fabrication, offering precise thickness control and superior conformality, particularly important for nanoscale structures. In this study, first-principles calculations based on density functional theory (DFT) were employed to investigate the catalytic role of silane (SiH_4) in the $TiCl_4/SiH_4/NH_3$ ALD process, with a focus on the removal of chlorine (Cl) atoms from the substrate surface. The results demonstrate that SiH_4 effectively promotes Cl desorption by reducing surface-bound Ti–Cl species, thereby enhancing surface reactivity and increasing the availability of active sites for improved precursor coverage. Detailed analyses of reaction pathways, activation energy barriers, and adsorption energies reveal that SiH_4 significantly lowers the energetic cost of Cl elimination, leading to a more efficient ALD process with higher growth-per-cycle (GPC) rates. These findings provide valuable insights into the catalytic mechanisms of SiH_4 and underscore its critical role in producing high-quality TiN films with reduced impurity levels. This work offers practical guidance for optimizing precursor combinations and process parameters in ALD technology.

9:30am **AF1-TuM-7 Correlation of Hydroxyl Group and Growth Characteristics in Atomic Layer Deposition of Ternary Oxide Depending on Growth Temperature*, Sanghun Lee,*** Yonsei University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea*; Hyungjun Kim,* Yonsei University, Republic of Korea

Atomic layer deposition (ALD) of doped or alloy materials has been intensively investigated with recent advances in nanotechnology applications. However, ALD of multicomponent materials is challenging because the growth characteristics often deviate from what is expected due to the difference in surface characteristics of heterogeneous and single materials, resulting in undesired thickness or properties. For metal oxides, the growth characteristics highly rely on the surface hydroxyl groups, which play a role as the reactive site. Thus, studying the reaction mechanism of a precursor on hydroxyl-terminated heterogeneous surfaces is important for understanding the nonideal growth of ternary oxide. This work provides understanding of how growth characteristics of ALD $TiSiO_x$ are deviated according to process temperature. Here, we investigated the correlation between hydroxyl and the growth of ALD $TiSiO_x$ depending on temperature, analyzing infrared spectra, and chemical compositions. The results show that large amounts of hydroxyl are detected in $TiSiO_x$ deposited at 100 °C, where the adsorption of H_2O on Ti–O–Si bonds is favorable. It leads to higher growth per cycle (GPC) than the estimated value. In contrast, hydroxyl disappears at 200 °C due to dehydroxylation, resulting in lower GPC. Differences in hydroxyl also influence the film density as revealed in x-ray reflection spectra, which is related to the film qualities (e.g., elastic modulus and dry etch rates). This work provides insight into how to control hydroxyl in the ALD of ternary oxides, which is susceptible to hydroxyl incorporation, leading to undesired growth characteristics.

9:45am **AF1-TuM-8 Atomistic Modeling of Oxygen Recombination Reactions in the ALD of SiO_2 and Al_2O_3*,*** *Suresh Kondati Natarajan,* Synopsys Inc., Denmark*; Rafshan Ul Atik,* Synopsys India Pvt. Ltd., India*; **Yong-Ju Kang**,* Synopsys Korea Inc., Republic of Korea*; Jess Wellendorff, Søren Smidstrup,* Synopsys Denmark ApS, Denmark

Atomic layer deposition (ALD) has been a key enabling technology for atomically fine-tuned manufacturing of cutting-edge semiconductor devices. Depending on the underlying chemical mechanism of the ALD process, growth rates can vary significantly from process to process. In semiconductor gate stacks, Al_2O_3 is considered as interface dipole inducer and SiO_2 has been used as gate oxide. It has been shown that plasma enhanced ALD (PEALD) growth rate of SiO_2 is orders of magnitude larger than that of Al_2O_3 [1]. In these processes, O_2 plasma is used as the source of oxygen. O_2 plasma includes reactive species such as O radicals which can, in principle, recombine with the previously deposited O species on the growth surface and form O_2 gas. It has been proposed that the growth rate difference between SiO_2 and Al_2O_3 can be attributed to the differences in the oxygen recombination rates at the respective growth surfaces [1].

In this talk, we present evidence from atomic scale modeling in terms of thermochemical, kinetic and dynamic analysis of reactions taking place at the SiO_2 and Al_2O_3 growth surfaces using industry-grade simulation frameworks within the QuantumATK software [2,3] developed by Synopsys. Dynamic simulations with Synopsys QuantumATK have been previously utilized to get insights and determine mechanisms of ALD of HfO_2 [4] and ALE of 2D TMD materials [5].

In this study, we employed Density Functional Theory to calculate the thermochemical and kinetic properties of oxygen recombination reactions at both SiO_2 and Al_2O_3 growth surfaces. Using thermochemical modelling, we computed the free energy change associated with oxygen recombination. Using kinetic modelling, we extracted the activation barrier for the recombination reaction and derived the corresponding reaction rates. MACE universal machine learned force field is chosen for dynamic simulations as *ab initio* methods are very time-consuming for such studies. Using dynamic modelling, we explicitly simulated the plasma species-surface interaction and compared the probability of recombination at both growth surfaces. From the results generated at different levels of atomic-scale modelling, we provide a comprehensive understanding of the oxygen recombination leading to growth rate differences observed in the PEALD of the two materials.

[1] K. Arts et al., J. Phys. Chem. C, 123, 27030−27035 (2019).

[2] QuantumATK V-2024.09, Synopsys. (https://www.synopsys.com/quantumatk)

[3] S. Smidstrup et al., J. Phys.: Conden. Matter 32, 015901 (2020).

[4] J. Schneider et al., ALD/ALE 2022, Ghent, Belgium.

[5] S. K. Natarajan et al., ALD/ALE 2024, Helsinki, Finland.

ALD Fundamentals
Room Halla Hall AB - Session AF2-TuM

Mechanism and Theory II

Moderators: Atsushi Sakurai, ADEKA CORPORATION, **Tania Sandoval**, Technical University Federico Santa Maria

10:45am **AF2-TuM-12 Screening Volatile Metal Complex for ALD Precursor by Modified COSMO-SAC Method and Estimating Its Reactivity by Atomistic Simulator Using Neural Network Potential***, **Noboru Sato,*** The University of Tokyo, Japan*; Naoyuki Hoshiya, Akiyoshi Yamauchi, Shigehito Sagisaka, Yosuke Kishikawa,* DAIKIN INDUSTRIES, LTD., Japan*; Yuxuan Wu, Jun Yamaguchi, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

The film growth characteristics of ALD vary greatly depending on the precursors; therefore, there are many attempts to develop novel metal complexes. We are developing a method to predict and measure metal complexes' vapor pressure and adsorption equilibrium constants for the ideal ALD precursor. As ALD utilizes the saturated chemisorption of the precursor, high vapor pressure and equilibrium constant are required. We established a method for accurately estimating the vapor pressures of metal complexes by modifying the COSMO-SAC (COnductor-like Screening MOdel - Segment ACtivity) method proposed by Lin et al [1, 2]. In this presentation, we report the results of predicting and developing metal complexes with high vapor pressures, and we analyze the reactivity of candidate compounds using an atomistic simulator based on neural network potential (Matlantis™). Calculations were performed using the PBE+D3 level of theory.

When investigating the conditions for high-vapor-pressure complexes, we found that the lower the polarizability and dielectric constant, the higher is the vapor pressure (Figure 1). Accordingly, we predicted the vapor pressure of Co complexes with a polarizability of 220 or less and a dielectric constant of 2.1 or less, the results are shown in Figure 2. When we synthesized $CpCo(C_2F_4)CO$ and measured its vapor pressure, we found it to be 8 Torr at 85°C, which is sufficiently high for ALD applications (Figure 3). Thus, by utilizing the COSMO-SAC method, it is possible to design metal complexes with high vapor pressures.

To evaluate whether $CpCo(C_2F_4)CO$ can be used for ALD, we used Matlantis™ to calculate the chemisorption process on the Cu(111) surface, which served as the growth substrate (Figure 4). The metal complex physisorbed with an energy of 90kJ/mol, and the Cp ligand dissociated with a low activation barrier of 10–25kJ/mol, suggesting that it can be readily adsorbed on a clean Cu(111) surface at 200–300°C. When calculating the adsorption energies of the CO, C_2F_4, and Cp groups, we found that while the CO and C_2F_4 groups have adsorption energies of 90kJ/mol, the Cp group exhibits a very high adsorption energy of 245kJ/mol. This indicates that removal of the Cp group is likely to be the rate-determining step. The effective removal of Cp groups from the surface remains a challenge for future work.

References

1. Lin S.T., et. al., *J. Phys. Chem. A*, **108** (2004) 7429-7439.
2. Sato, N., et. al., AVS 24th International Conference on Atomic Layer Deposition, Helsinki, Finland (2024), AF1-TuM-2.

11:00am **AF2-TuM-13 Ion Effects on Plasma-induced Surface Composition Changes during SiCN Atomic Layer Deposition: A Combined Ab-Initio and Monte Carlo Approach***, **Ting-Ya Wang,*** University of Texas at Austin, Taiwan*; Hu Li,* Tokyo Electron America, Inc., China*; Peter Ventzek, Jianping Zhao,* Tokyo Electron America, Inc.*; Gyeong Hwang,* University of Texas at Austin, Korea (Democratic People's Republic of)

Plasma-enhanced atomic layer deposition (ALD) is an effective method for reducing deposition temperatures, particularly during nitridation. However, plasma can also introduce adverse effects, such as altering chemical composition and causing densification, which significantly influence key material properties like the dielectric constant. Understanding plasma-induced changes in surface morphology and composition is therefore critical. While experimental techniques for surface analysis face inherent limitations, theoretical methods also present challenges, particularly in modeling ALD processes where primary surface reactions are rare events.

Integrating kinetic Monte Carlo (kMC) with density functional theory (DFT) offers a powerful approach for simulating ALD. However, a key challenge in kMC lies in the need for a predefined list of permissible events. Traditionally, researchers manually compile a set of reactions deemed most significant. Yet, the vast number of possible events on a surface, combined with the importance of rare events in ALD, raises concerns about the authenticity and completeness of outcomes derived from manually curated reaction lists.

We developed an atomistic, off-lattice, three-dimensional simulator that integrates kMC with DFT. We employed a strategic approach to construct a comprehensive event list, capturing a broad spectrum of potential surface reactions. Our study focused on investigating the effects of ions in N_2 plasmas on silicon carbonitride (SiCN) materials, with particular emphasis on the roles of ion energy and flux.

SiCN is a low-k material critical for semiconductor manufacturing, where low dielectric constants are essential to minimize capacitive coupling in integrated circuits. The dielectric properties and mechanical strength of SiCN are strongly influenced by the elemental composition, bond types, and bond orders. Variations in these parameters can lead to significant differences in film quality and functionality, highlighting the importance of understanding and controlling these characteristics. By utilizing our simulator to model surface reactions and the evolution of SiCN films during ALD, we aim to validate and refine our approach while identifying strategies to optimize the material's properties for industrial applications.

11:15am **AF2-TuM-14 Benchmarking Large Language Models for Atomic Layer Deposition***, **Angel Yanguas-Gil,** Matthew Dearing, Jeffrey Elam, Jessica Jones, Sungjoon Kim, Adnan Mohammad, Chi Thang Nguyen, Bratin Sengupta,* Argonne National Laboratory

In this work we introduce an open-ended question benchmark, ALDbench, to evaluate the performance of large language models (LLMs) in the field of atomic layer deposition. Our benchmark comprises questions with a level of difficulty ranging from graduate level to domain expert current with the state of the art in the field. Human experts reviewed the questions along the criteria of difficulty and specificity, and the model responses along four different criteria: overall quality, specificity, relevance, and accuracy. We ran this benchmark on an instance of OpenAI's GPT-4o using an API interface. This allows us to fine tune hyperparameters used by the LLM for text generation in a way that is not possible using conventional chat-based interfaces.

The responses from the model received a composite quality score of 3.7 on a 1 to 5 scale, consistent with a passing grade. However, 36% of the questions received at least one below average score. An in-depth analysis of the responses identified at least five instances of suspected hallucination. We also observed statistically significant correlations between the following question and response evaluation criteria: difficulty of the question and quality of the response, difficulty of the question and relevance of the response, and specificity of the question and the accuracy of the response. Finally, we will address other issues such as reproducibility, impact of hyperparameters on the quality of the response, and possible ways in which the performance of the LLMs can be further improved.

[1] Yanguas-Gil et al, Benchmarking large language models for materials synthesis: the case of atomic layer deposition, arXiv:2412.10477 (2024). Submitted to JVSTA

11:30am **AF2-TuM-15 Adsorption State Study of Trimethylaluminum Using Neural Network Potential Computation and High Accuracy in-situ Quartz Crystal Microbalance***, **Yuxuan Wu,*** The University of Tokyo, Japan, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic layer deposition (ALD) is primarily applied in ULSI fabrication because of its characteristics of alternately supplying the precursor and reaction gas, relying on saturation of surface adsorption. This results in excellent uniformity and stability of the film thickness against fluctuations in fabrication conditions. Detailed results from previous studies have constructed a well-defined adsorption and reaction pathway for TMA ALD by in-situ characterization and computational simulation. The growth of Al_2O_3 could be understood by the adsorption amount and structures of TMA and H_2O at each step, where the $-CH_3$ and -OH densities on the surface significantly determine the characteristics of deposition. Understanding such termination on the surface can reveal the thermodynamic and kinetic factors for the reaction, where the quality and efficiency of the reaction can be controlled.

Conventional methods, such as Density Functional Theory (DFT) and Quartz Crystal Microbalance(QCM), examine the surface adsorption and reaction of precursors. However, the challenges of time-consuming and inapplicable for the steric hindrance prediction with a large slab size remain for DFT, and the insufficient accuracy of QCM (1 ng/cm^2) limits the measurement of small molecule adsorption. These limitations influence the analysis of the surface adsorption of TMA.

Using a state-of-the-art simulator (Matlantis$^{\text{TM}}$) with the Preferred potential (PFP) and high-accuracy in-situ QCM with a calibrated frequency counter and resonator, we explored the adsorption and reaction of TMAon the Al_2O_3 surface. Because of the precise neural network potential (PFP) developed by advanced machine learning-based techniques, it can easily predict the adsorption behavior of precursors on large adsorption surfaces in an extremely short time (minutes). We calculated the adsorption state and energy for TMA using Matlantis$^{\text{TM}}$ and found good agreement with previous DFT calculations, as shown in Fig.1 (<0.07 eV). The adsorption calculation later expanded to multiple TMA molecule adsorption on the surface and predicted surface coverage for TMA by the steric hindrance effect due to the methyl group as 0.75, compared with the reference predicting surface coverage of 70%–80%. The adsorption amount of TMA on the Al_2O_3 surface with predicted surface coverage is 34.7 ng/cm^2, which is close to the experimental results from modified in-situ QCM, which shows 40 ng/cm^2 with a crystal roughness of 15%. The results from jMatlantis$^{\text{TM}}$ were predicted well and precisely compared with both experiment results from QCM and computational DFT.

11:45am **AF2-TuM-16 Atomistic Insights into the Surface Chemistry Driving ALD of IGZO Films from First-Principles and Machine-Learning Simulations*, Alex Watkins,*** University of Warwick, UK

The quaternary oxide semiconductor In-Ga-Zn-O (IGZO) has gained attention in recent years due to its promise in key properties: high optical transparency, high electron mobility, and low fabrication costs. These properties make it an exciting candidate for several applications including thin-film transistors (TFTs) in next-generation OLEDs, flexible electronic devices, advanced CMOS, and AI hardware.[1] One technique that has become indispensable for thin-film fabrication such as this is ALD, due to its exceptional conformality and control. The ALD process of IGZO requires a complex supercycle consisting of three single-component steps, each requiring a three-step process. This complexity requires significant optimisation to have success, this is where understanding the underlying surface chemistry is key, and atomistic simulations can provide great assistance.

In ALD the initial nucleation of a precursor on a target substrate is key to the overall quality of the deposited film, this requires effective precursor binding to the surface. Molecular dynamics (MD) simulations and minimum-energy reaction pathway analysis, enabled by *ab initio* Density Functional Theory (DFT) offer valuable insights into reaction chemistry, shedding light onto kinetics and thermodynamics factors.[2,3,4,5,6,7,8] Most recently machine-learned interatomic potentials (MLIPs) offer a major boost to the capabilities of these simulations, in bridging the gap between atomistic simulations studying binding of a single precursor and the kinetic Monte Carlo simulations studying larger scale properties such as rates of deposition and surface coverage.

In this contribution, we will present key atomistic insights into the ALD nucleation and growth mechanisms of IGZO on silicon oxide (SiO_2) substrate, as predicted by DFT and MLIPs, considering the different ALD sub-cycles, e.g. InOx, GaOx and ZnOx depositions. In particular, we will discuss the effect of simultaneous substrate binding of multiple precursors/co-reactants on the nucleation and growth behaviour, and the effect of temperature on the adsorption and surface coverage properties.

[1] *ACS Applied Electronic Materials* **2024,** 6 (8), 5694-5704; [2] *ACS Nano* **2017**, 11, 9, 9303–9311; [3] *Chem. Mater*. **2019**, 31, 4, 1250–1257; [4] *Chem. Mater*. **2017**, 29, 3, 921–925; [5] *Nanoscale*, **2021**, 13, 10092-10099; [6] *Chem. Mater*. **2017**, 29, 5, 2090–2100; [7] *Nanoscale*, **2016**, 8, 19829-19845; [8] *Solar Energy Materials and Solar Cells* **2017**, 163, 43-50.

ALD Fundamentals

Room Tamna Hall B - Session AF3-TuM

Precursor Chemistry II

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

8:00am **AF3-TuM-1 ALD of SnO_2 Thin Films using Tin(IV) Acetate as a Novel Precursor*, Anjan Deb*,** *Miika Mattinen, Mikko J. Heikkilä, Mykhailo Chundak, Anton Vihervaara, Kenichiro Mizohata, Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

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

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

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

8:15am **AF3-TuM-2 Bridging the Gap: Volachem's Mission to Advance ALD Precursor Development*, Martin Wilken*,** *Dominik Naglav-Hansen, Andreas Ostendorf,* Ruhr Universität Bochum, Germany*; Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

The development of new precursors is essential for expanding atomic layer deposition (ALD) applications in microelectronics and beyond.[1-2] However, a persistent challenge remains: the limited availability of precursors that combine high volatility, high reactivity and thermal stability, and while meeting industrial scalability requirements. The transition from cutting-edge scientific research to commercially available precursors is particularly difficult, with only a few dedicated R&D projects and companies addressing this gap. This is where VolaChem steps in.

VolaChem, founded by Dr. Dominik Naglav-Hansen and Dr. des. Martin Wilken, is a science-to-market transfer project dedicated to the development of volatile chemicals for technical applications. A key focus is the research, development, and up-scaling of ALD precursors, ensuring their applicability in the processing of advanced materials. By employing a database-driven approach for synthesis R&D, specialized precursor analytics, and consulting services, VolaChem aims to accelerate the transition of novel precursor concepts from academia to industry.

In this presentation, the authors will introduce their business concept and service offerings as well as innovative methodologies, while fostering a scientific dialogue on the needs, challenges, and opportunities related to volatile compounds in both research and industrial settings.

VolaChem is built upon the founders' extensive academic research and expertise in designing tailored compounds for use as volatile precursors in technical processes.[3-6] By bridging the gap between laboratory innovation and industrial application, VolaChem aspires to become a driving force in the next generation of ALD chemistry.

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

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

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

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

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

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

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2. Gan Liu, *et al.*, *VLSI2024*, T16-1
3. Junghwan Kim, Jin-Seong Park, *et al.*, *ACS Appl. Mater. Interfaces* **2019**, 11, 43, 40300

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

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

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

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

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

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

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

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

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

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

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

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

ALD Fundamentals
Room Halla Hall AB - Session AF1-TuA
Analysis

Moderators: Christophe Detavernier, Ghent University, Belgium, **Adrie Mackus**, Eindhoven University, Netherlands

1:30pm **AF1-TuA-1 Interface Evolution in ALD of HfO_2 on TiN: LEIS and XPS in Vacuo Studies***, **Mykhailo Chundak**, Heta-Elisa Nieminen, Marko Vehkamäki, Laura Keränen, Matti Putkonen, Mikko Ritala,* University of Helsinki, Finland

Hafnium dioxide (HfO_2) is a high-k dielectric material that was initially introduced as a replacement for SiO_2 to overcome the scaling limitations of silicon-based field-effect transistors. HfO_2 has therefore been qualified as a material compatible with complementary metal oxide semiconductor (CMOS) technology. It has recently regained attention following the discovery of ferroelectricity in doped hafnium oxide fluorite-structure oxides. This discovery has enabled the development of ferroelectric field-effect transistors (FEFETs) and ferroelectric memories, which offer the potential for further downscaling of CMOS-compatible ferroelectric based devices. However, as the thickness of ferroelectric layers is decreased from the current 5–10 nm to approximately 3 nm or even less, their properties become increasingly influenced by the surrounding environment, making precise interface engineering crucial for device reliability. The choice of the capacitor electrode plays a key role in stabilizing the ferroelectric phase, mitigating interfacial effects, and ensuring long-term performance. Titanium nitride (TiN) is widely employed due to its moderate work function, chemical stability, and compatibility with CMOS technology, yet its interaction with ultrathin HfO_2 films, along with potential contamination and deposition conditions, can significantly impact device behavior. A detailed understanding of these effects is therefore essential to optimize material integration and enhance the performance of next-generation semiconductor devices.

To investigate the growth of these films using surface science techniques, we utilized the cluster tool setup in the HelsinkiALD laboratory[1] (Fig. 1a)). This system enables *in vacuo* growth studies, providing direct insights into surface reactions during deposition. We employed a commercial flow-type ALD reactor combined with low-energy ion scattering (LEIS) (Fig. 1b)) and X-ray photoelectron spectroscopy (XPS) (Fig. 1c)) to observe the cycle-by-cycle growth of HfO_2 thin films. The films were deposited with $CpHf(NMe_2)_4$ (HyALD$^{\text{TM}}$) precursor in combination with ozone (O_3) on TiN substrate. This approach provided critical information of the interface formation and film growth mechanisms. We determined that ~30 ALD cycles are required to achieve full coverage of HfO_2 on TiN without pinhole defects. This research is offering a valuable information for optimizing thin-film deposition for next-generation semiconductor technologies.

1. Nieminen, H.-E., et al., *In vacuo cluster tool for studying reaction mechanisms in atomic layer deposition and atomic layer etching processes.* Journal of Vacuum Science & Technology A, 2023. **41**(2).

1:45pm **AF1-TuA-2 In Situ Ambient Pressure X-ray Photoelectron Spectroscopy Study of Atomic Layer Deposition of Hafnium Oxide on (Ag,Cu)(In,Ga)Se_2 Absorbers Relevant for Thin Film Solar Cells***, **Natalia M. Martin**,* Uppsala University, Angstrom Laboratory, Sweden

Thin film solar cells based on (Ag,Cu)(In,Ga)Se_2 (ACIGS) absorbers have reached efficiencies of up to 23.6%, which together with demonstrated long term stability has set the basis for commercial application. To reach closer to the theoretical maximum efficiency (~30%), further reductions of optical and electrical losses are needed. One of the most critical parts in ACIGS-based solar cells is the interface formation between the p-type absorber and n-type (buffer) layer forming the pn-junction. Energy band alignment at this interface is a key parameter, but also absorber surface band gap widening, interlayer formation and distribution of alkali trace elements. In addition, the deposition of ultrathin barriers of HfO_x has previously been investigated in Cu(In,Ga)Se_2 (CIGS) thin film solar cells and shown to be an effective passivation layer by reducing interface recombination with an appropriate contacting approach. However, the ALD HfO_x growth on ACIGS has not truly been explored and the surface chemistry and reactions occurring on the ACIGS absorber surface during HfO_x deposition are unknown. An important step towards achieving superior device performance is to understand the chemical reactions occuring during the first deposition cycles of HfO_x, which could result in better interface quality, and to ultimately design better solar cells.

We employed ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to study how the surface properties of ACIGS and how the reaction between ALD precursors and the ACIGS surface proceed during the deposition of HfO_x. ACIGS thin films of similar bulk composition, with and without a surface treatment were compared. Using *in situ* AP-XPS, we followed in real time the reactions occurring during the initial ALD of HfOx on ACIGS. The results show that the ACIGS surface plays an important role in the initial ALD surface chemistry, with surface hydroxyls, fluorine and alkali elements that may exert significant influence on the surface chemistry during the initial TDMA-Hf half-cycle. Whereas the HfOx growth occurs directly upon a short TDMA-Hf pulse on a non-treated ACIGS surface, an increase in the induction/coalescence time period at the beginning of ALD is observed for a RbF-treated ACIGS, likely due to the presence and diffusion of Rb and F to ACIGS surface, limiting the surface diffusion of O-containing species, i.e. the available sites for TDMA-Hf molecule to adsorb and react on, or even the lower oxide amount present on the surface before the ALD growth. Understanding the ALD reaction mechanism, especially during the initial growth of HfOx on ACIGS is crucial to improving interface properties in ACIGS-based devices.

2:00pm **AF1-TuA-3 Development of a Home-Built Atomic Layer Deposition Reactor for *in-Situ* Synchrotron GISAXS and XAS Characterization***, **Marina Armengol-Profitós**, Jordi Prat, Montserrat Prieto, Zbigniew Reszela, Cristián Huck-Iriart, Massimo Tallarida, Eduardo Solano, Carlos Escudero,* ALBA synchrotron light source, Spain

The high photon flux and energy tunability of synchrotron facilities provide a clear advantage for the characterization of Atomic Layer Deposition (ALD) processes. At the ALBA synchrotron, a mobile custom-built reactor has been developed to enable in-situ monitoring of film growth and characterization using up to now two X-ray-based techniques: Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) and X-ray Absorption Spectroscopy (XAS). The ALD reactor has been designed to be compatible with both techniques, and it can currently operate at two different ALBA beamlines (NCD-SWEET for GISAXS measurements and NOTOS for XAS) to provide complementary insights into film morphology and chemical composition.

The setup consists of a high-vacuum, pump-type reactor compatible with multiple deposition processes. It achieves a base pressure of at least 10^{-6} mbar and is equipped with a sample heater capable of reaching 1000°C, allowing in-situ annealing under different atmospheres without exposing the sample. To accommodate the specific geometries required for each X-ray technique, the mobile reactor features two different configurations: for GISAXS, two CF40 flanges with mica windows allow the passage of incident and reflected X-rays, while for XAS, two perpendicularly oriented flanges with 50 µm-thick Kapton windows enable measurements covering all the beamline energy range (4.7 - 30 keV), with the fluorescence detector used (SDD with 13 channels) at 90° relative to the X-ray beam and the sample at around 30° with respect to the incident beam. Fig. 1 A shows the reactor in the GISAXS configuration at the NCD-SWEET beamline.

To validate the reactor's performance, TiO_2 thin films were deposited using titanium isopropoxide (TTIP) as a precursor in combination with water on SiO_2/Si substrates. The process exhibited a growth rate of 0.15 Å/cycle, allowing the study by GISAXS and XAS in the sub-nanometer range during the initial growth cycles. Fig. 1 B presents XANES measurements at the Ti K-edge over 1000 ALD cycles at 200°C, revealing an increase in the XANES-edge jump intensity within the first five cycles. Since the edge jump magnitude is proportional to the TiO_2 thickness, these results indicate different growth regimes: a first stage significantly slower for 325 cycles, followed by a stage where the growth rate becomes linear. After 325 cycles, XAS measurements confirmed the formation of TiO_2 with features consistent with anatase-like coordination. The XANES features during the first 325 cycles are consistent with previously studied electronic effects in ultra-thin TiO_2 films[1]. Additionally, XAS mapping over a 20 mm x 20 mm area validated the film's uniformity.

2:15pm **AF1-TuA-4 Evaluation of Initial Nucleation of Co-ALD by CCTBA Using in-Situ Reflectance Monitoring and Atomistic Simulator Based on Neural Network Potential***, **Naoki Tamaoki**,* The University of Tokyo, Japan*; Yubin Deng,* The University of Tokyo, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Area-selective atomic layer deposition (AS-ALD) technology, which enables atomic-level control of the film thickness and inherently prevents misalignment in self-aligned patterning, is gaining attention in ULSI device manufacturing. AS-ALD utilizes the difference in the adsorption energies of the precursor molecules to deposit a film only on the growth surface. It is crucial to explore the surface pretreatment and process conditions that maximize the incubation time to improve selectivity. In-situ differential reflectance spectroscopy (DRS) is a simple and effective method that assists in this exploration by monitoring the nucleation density and film growth evolution during the initial deposition stages. To better understand the mechanism of AS-ALD, in-situ DRS and an atomistic-level simulator (Matlantis™) based on neural network potentials were used to study Cobalt ALD.

In this study, the initial growth process of Co thin films on SiO_2 insulating films using CCTBA (Cobalt Carbonyl Tertiary-Butyl Acetylene) precursors via ALD was evaluated. Co AS-ALD is expected to be a promising method for forming cap layers that suppress Cu diffusion and electromigration (EM) in ULSI-Cu interconnects. After APM cleaning, Co-ALD was performed for 500 cycles at different substrate temperatures (140, 150, and 160°C), and the reflectance changes at a wavelength of 740 nm were measured (Figure 1). The reflectivity gradually decreased as the island-like growth of Co began, reaching a minimum value before increasing again. By analyzing the timing of the minimum reflectivity, it is possible to determine when the initial nuclei form and evolve into a continuous film [1]. Figure 2 shows the growth per cycle (GPC) measured after film formation as an Arrhenius plot. Figure 3 shows the Arrhenius plot of the initial nucleation density calculated from the minimum reflectance point and GPC data. While GPC exhibited a mild temperature dependence with an activation energy of 14.6 kJ/mol, the initial nucleation density showed a relatively high activation energy of 100.5 kJ/mol. Although lowering the film-formation temperature may increase the concentration of carbon impurities in the film, it is expected to suppress the initial nucleation density and improve the selectivity. We will also report the results of the reaction analysis using an atomistic-level simulator (Matlantis™).

[1] N. Tamaoki et al., DPS 2024

2:30pm **AF1-TuA-5 Low Energy Ion Scattering Analysis of GC/IrOX /SiO_2 Layer Structure**, ***Philipp Brüner***, *Thomas Grehl,* IONTOF GmbH, Germany*; Rens Kamphorst, Katherine S. Encalada Flores, Ruud Kortlever, Ruud van Ommen,* TU Delft, Netherlands

While ALD with its self-limiting properties and sub-nm precision provides an ideal method for growing ultra-thin coatings, the physical and chemical characterization of the obtained films is challenging for surface analytical methods. Especially for ultra-thin films consisting of only few atomic layers or even a sub-monolayer only, most analytical techniques suffer from their limited surface sensitivity, often including, and thus averaging over, both the deposited film and the growth substrate.

In this study, we present analytical results of low energy ion scattering (LEIS) applied to SiO_2 films grown by ALD on an electrodeposited IrO_x catalyst layer on glassy carbon (GC). In LEIS, the energy spectrum of noble gas ions (He, Ne, Ar) scattered from the sample surface is recorded. The elemental peaks in the resulting spectra represent the elemental composition of the first atomic layer, which can be analyzed quantitatively [1]. This extreme surface sensitivity of just a single atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of ultra-thin films. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm, depending on the sample composition.

We show how combining the top atomic layer sensitivity with layer thickness information allows us to quantify the surface coverage of the deposited SiO_2 films, identify surface impurities with high sensitivity, and make a statement about the growth mode of the films. While ALD should in theory grow films in a perfectly controlled layer-by-layer manner [2], the deposited films often show various degrees of island growth, where parts of the substrate are quickly covered by a multilayer film, while other parts of the substrate have not yet begun to initiate film growth.

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2:45pm **AF1-TuA-6 Tailoring Interface and Bulk Properties: An Oxidant Co-Dosing Approach to ALD Growth of Hafnia Thin Films**, ***Dushyant Narayan***, *Dan Le, Soham Shirodkar, Soubhik De, Geon Park, Minjong Lee, Thi Thu Huong Chu, Jin-Hyun Kim,* The University of Texas at Dallas*; Walter Hernandez, Adrian Alvarez, Josh Garretson, Jeffrey Spiegelman,* RASIRC*; Jiyoung Kim,* The University of Texas at Dallas

As semiconductor devices continue to scale down and integrate into complex 3D architectures, precise control over interfacial properties becomes increasingly critical to device performance and reliability. Hafnia-based thin films have been widely adopted in industry, as they exhibit superior equivalent oxide thickness (EOT), high dielectric constant and superior leakage current properties as compared to traditional dielectrics like SiO_2. These attributes make HfO_2-based materials essential for applications such as high-k gate dielectrics, DRAM capacitors, and ferroelectric memory devices.

In our prior studies investigating the impacts of various oxidant sources on HfO_2-based films, we found that the conventional ozone (O_3)-based ALD process led to extensive oxidation of the titanium nitride (TiN) bottom electrode (BE) during metal-insulator-metal (MIM) capacitor fabrication. In contrast, the use of hydrogen peroxide (H_2O_2) in HfO_2-based ALD was not only shown to produce films with superior growth characteristics and material properties, but also effectively suppressed unwanted interface formation.[1] Building upon these findings, we have developed a unique ALD approach, where oxidants (H_2O_2, O_3, and H_2O) are strategically co-dosed/sequentially-dosed to achieve a greater control of film properties.Through this process, customizable ALD growth conditions can provide tailored properties at the interface and in the bulk. Furthermore, results of an *in-situ* Reflection Absorption Infra-Red Spectroscopy (RAIRS) experiment will be presented, investigating the underlying mechanisms at the surface and in the bulk when mixing oxidants during the deposition of hafnia. For instance, While H_2O_2 on its own produces film with superior properties, it is not known if mixing O_3 and H_2O_2 would further enhance material properties. Additional combinations including H_2O, O_3 and H_2O_2 will also be shown. Beyond IR analysis, we will also present the effect of this approach on electrical properties of hafnia thin films, with particular attention paid to dielectric constant, leakage current, and time dependent dielectric breakdown (TDDB). This study thus represents an additional process variable that can be utilized to further optimize the use of HfO_2-based materials in next-generation device applications. Detailed experimental procedure and results will be discussed.

This work is supported by RASIRC. The BRUTE® Peroxide and RASIRC Peroxidizer® are provided by RASIRC Inc. The O_3 used in this work was provided by a TMEIC Ozone Generator (OP-250H).

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3:00pm **AF1-TuA-7 Mechanical Properties and Wear Resistance of Atomic Layer Deposited Ternary Cr-Hf-O Films: A Comparative Study with Binary Chromium Oxide and Hafnium Oxide Films**, ***Mahtab Salari Mehr***, *Lauri Aarik, Taivo Jõgiaas, Hugo Mändar,* University of Tartu, Estonia

The complex materials including doped and ternary compounds have received considerable attention in the last decades due to the exhibition of superior mechanical, optical, and electrical properties compared to their binary counterparts. [1,2]. Chromium oxide is technologically an important engineering material due to its corrosion, wear resistance, and high mechanical hardness [3,4].This study presents the characterization results of ternary chromium-hafnium oxide films ((Cr1-xHfx)2O3) in thickness range from 40 to 80 nm that were deposited at 275 °C on Si substrate by atomic layer deposition (ALD) using the cycle formula of [*m* ($Cr(thd)_3$-O_3) + ($HfCl_4$-O_3), *m*=0 to 500]. The X-ray fluorescence showed the change in atomic ratio of Hf/(Hf+Cr) (*x*) in the films from 0.05 to 1 by changing *m* in the ALD cycle. Grazing incidence X-ray diffraction analysis of pure hafnium oxide film showed reflections of the monoclinic phase, whereas for pure chromium oxide film the observed reflections confirmed the presence of the eskolaite phase. For the $(Cr_{1-x}Hf_x)_2O_3$ films when $0.05 \le x \le 0.40$, the eskolaite phase was present, however, the films containing $x \ge 0.68$ showed semi-amorphous structure. The density of the films (from X-ray reflectivity analysis) showed a linear increase from 5.57 g/cm^3 to 10 g/cm^3 when the amount of *x* changed from 0.05 to 1. The hardness, elastic modulus, and wear resistance of the films were measured using nanoindentation on Hysitron Triboindenter by Berkovich-type diamond tip. The results at indent displacement of 8 nm showed an increase in hardness mean values of ternary films compared with binary chromium oxide (14±1.5 GPa) and hafnium oxide (12±1.2 GPa). The highest hardness of 19±0.9 GPa was achieved when *x*=0.40. The study of wear resistance of the films under different loads in the range of 90 to 180 µN, using different wear cycles of 2 to 10 cycles showed an improvement of about ~70% of wear resistance of the ternary compound films compared to binary oxides (Fig. 2). Our findings showed that the deposition of multicomponent films paves the way for tailored thin film materials with enhanced mechanical properties and wear durability for various industrial applications.

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3:15pm **AF1-TuA-8 In-situ X-ray photoelectron spectroscopy for determining oxidation state, composition, and morphology of ALD-based CeO_x, SnO_x, and $Ce_xSn_{1-x}O_y$ deposits*, Rudi Tschammer*,** *Dominic Guttmann,* BTU Cottbus, Germany*; Marcel Schmickler, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany*; Karsten Henkel, Carlos Morales, Jan Ingo Flege,* BTU Cottbus, Germany

The controllability of the physical and chemical properties of ultrathin (< 20 nm) films grown by atomic layer deposition (ALD) requires a thorough understanding of the surface cross-interactions established between substrates, grown thin films of variable thickness, and the exposed reactants. In most ALD works focused on applications, samples are grown in dedicated ALD reactors on wafer-scale substrates and characterized through various *ex-situ* techniques to obtain information on film thickness, sample composition, and cation valency. However, *ex-situ* characterization bears the risk of unintentional changes due to layer contact with the atmosphere, ranging from surface contamination to changes in the surface cation oxidation state. The latter issue is especially pronounced for reducible oxides intended to switch between different oxidation states depending on factors such as gas environment or film-substrate interaction (e.g., CeO_x, widely used in catalysis and sensing). Thus, a surface science methodology supported by *in-situ* characterization becomes highly desirable to minimize changes imparted during sample transfer in the atmosphere and unravel the true structure and chemical state of the pristine active layer.

In this contribution, we examine the material composition, cation valency, and film morphology through *in-situ* X-ray photoelectron spectroscopy (XPS) and inelastic peak shape analysis (IPSA) combined with operando spectroscopic ellipsometry. By investigating the ALD deposition of CeO_x using $Ce(dpdmg)_3$ and different oxidants (H_2O, O_2, O_3), we observe a distinct dependence of the cerium valency on the film thickness and the used oxidant, in all cases accompanied by changes in film morphologies and precursor residues. Similarly, a detailed XPS analysis of the early stages of SnO_2 deposition via TDMASn/O_3 reveals hitherto unreported changes that could be correlated with residual nitrogen impurities, significantly influencing the electrical resistivity of these films. Following a bottom-up approach, the results from both investigations are combined to tailor the growth of ultrathin SnO_x/CeO_x heterostructures and mixed $Ce_xSn_{1-x}O_2$ oxides for gas sensing applications.

ALD Fundamentals
Room Halla Hall AB - Session AF2-TuA
Plasma ALD

Moderators: Ruud van Ommen, Delft University of Technology, **Seung-Yeul Yang**, Samsung

4:00pm **AF2-TuA-11 Controlling the Crystalline Nature of PEALD Thin Films Through Tuning of Plasma Characteristics*, Peter Litwin,*** Naval Research Laboratory, USA*; Marc Currie, Neeraj Nepal, Maria Sales, David Boris,* US Naval Research Laboratory*; Michael Johnson,* Naval Research Laboratory, USA*; Scott Walton, Virginia Wheeler,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) utilizes a plasma-based reactant step increasing the complexity of the deposition process compared to thermal ALD. The plasma-based reactant step introduces a flux of energetic particles (ions, fast neutrals, electrons, photons, etc.) directed towards the surface of the growing thin film, which helps reduce the energetic barriers to high growth rates or crystallinity at low temperatures. Understanding the role that these energetic species play in the deposition process potentially enables better tunability of the growth conditions for a given application. For example, during the plasma step, careful control of the power, pressure, gas flow mixture, and substrate bias all enable control over the magnitude of the ion energy flux density delivered to the sample surface. The consequence of this is a greater level of control over the properties of the deposited material. This has been experimentally observed in previous studies, namely in the control of the crystalline phase of various compounds. For example, through alteration of the gas chemistry, flow rate, and pressure used during the reactant half-step it has been shown that the rutile and anatase phases of TiO_2 and the α- and β-phases of Ga_2O_3 could be selectively deposited [1, 2].

In this work, we investigate methods to vary the properties of the plasma in our PEALD system. We use a suite of characterization techniques, including optical emission spectroscopy (OES) and Langmuir probe measurements, to examine how various plasma conditions (power, pressure, and gas flow ratio) impact the ion flux, plasma potential, and atomic O concentrations produced in our Kurt J. Lesker 150 LX PEALD system. As a testbed, we deposit vanadium oxide and report on how the changing properties of the plasma impact the properties of the deposited thin films. We find that through alteration of the pressure in the system during the plasma process, the films can be selectively deposited in an amorphous or crystalline manner. We correlate this change in crystallinity with the change in the energy flux density delivered to the material surface during deposition. From this, we estimate the critical energy flux density necessary for crystallization of vanadium oxide films deposited in our PEALD system. Lastly, we discuss these results more broadly and consider the applicability of these findings to other material systems.

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4:15pm **AF2-TuA-12 Comparative Study of CeO_2 Thin Films Prepared by Plasma-Enhanced and Thermal Atomic Layer Deposition Using a New Liquid Ce Precursor*, Yewon Seo,*** *Sang Bok Kim, Soo-Hyun Kim,* Graduate School of Semiconductor Materials and Devices Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea

Cerium oxide (CeO_2) has been widely studied for applications such as optical waveguides, solid oxide fuel cells (SOFCs), and gas sensors. In particular, it is considered a promising gate dielectric material for complementary metal-oxide-semiconductor (CMOS) devices due to its high dielectric constant (23–52), high refractive index (2.2–2.8), excellent dielectric strength (25 MV/cm), moderate bandgap (3.0–3.6 eV), and thermodynamic stability in contact with silicon [1]. So far, research on ALD CeO_2 films, especially plasma-enhanced ALD (PEALD) of CeO_2, has been very limited, mainly due to the lack of suitable precursor-reactant combinations; thus, more detailed investigations are required. In this study, CeO_2 thin films were deposited by ALD using a new liquid Ce precursor with O_2 molecule or O_2 plasma as reactants. The deposition process was conducted at temperatures ranging from 150 to 350 °C, and both thermal ALD (Th-ALD) and PEALD exhibited self-limiting surface reactions at 250 °C.In addition, increases in peak intensities for PEALD CeO_2 film as compared to that of Th-ALD one were confirmed through XRD analysis (figure 1), indicating the improvement of the film crystallinity by using plasma as a reactant. Film properties varied with deposition conditions such as growth temperature, plasma power, reactant pulsing time, etc..and were characterized by SEM (thickness), TEM (step coverage, microstructure), XRR (density, thickness, roughness), XRD (crystallinity), and XPS (composition and impurity) etc. Electrical properties were evaluated via Metal–Oxide–Semiconductor capacitors, focusing on dielectric constant and leakage current. The detailed results will be presented at the conference.

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Acknowledgements

This work was also supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program (K-CHIPS) to foster high-quality human resources) (RS-2023-00232222, High-temperature atomic layer deposition precursors and processes for dielectrics in 3D V-NAND devices) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (1415187363) (RS-2024-00443041, Development of process parts based on atomic layer deposition technology of plasma coating materials) This work was also supported by the Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0023703, HRD Program for Industrial Innovation). The precursor used in this study was provided by UP Chemical Co. Ltd, Korea.

4:30pm **AF2-TuA-13 Tuning Crystallinity of Plasma-Enhanced Atomic Layer Deposited Aluminum Nitride Thin Films using an Electron Cyclotron Resonance Microwave Source***, **Julian Pilz**, Tai Nguyen,* Silicon Austria Labs, Austria*; Paul Dreher,* Evatec AG, Switzerland*; Marco Deluca,* Silicon Austria Labs, Austria

Aluminum nitride (AlN) thin films are widely utilized in microelectronic devices as high thermal conductance heat spreaders, piezoelectric actuators and sensors or high-k dielectrics.[1,2] In most applications, (0002)-textured wurtzite films are required to achieve the desired device performance.[3] While deposition techniques such as metalorganic chemical vapor deposition[4] and reactive magnetron sputtering[5] have demonstrated to produce highly textured/epitaxial films with low mosaic spread, these deposition techniques faces severe issues such as CMOS-incompatibility due to high temperature growth and poor conformality. Atomic layer deposition (ALD) is renowned for precise control of atomic arrangement and excellent conformality. However, achieving AlN with comparable crystal quality by ALD on Si substrates remains challenging and is under investigation [6,7,8], with factors such as oxygen and carbon contaminations shown to decrease the crystal quality.[9,10]

In this work, AlN thin films are deposited on 200mm Si(111) wafers by plasma-enhanced atomic layer deposition (PE-ALD) utilizing trimethylaluminum (TMA) and NH_3-plasma as reactants. A novel ALD module is used for the deposition of the films (Evatec PEALD), which utilizes an electron cyclotron resonance microwave source and is *in-vacuo* connected in a cluster tool to etch and sputtering modules, with the potential to overgrow and surface pretreat wafers without vacuum break, respectively. The focus of this work is to investigate how NH_3 plasma parameters (pressure, power, duration) produced by the microwave source influence the plasma/chemical species during deposition and resulting thin film properties in terms of thickness uniformity, crystallinity, roughness, and chemical composition. For example, while films grown with 2 s NH_3-plasma duration showed similar growth per cycle values as films grown with 5 s plasma duration, they appear amorphous and structurally unstable in atmosphere. Increase of plasma duration up to 20 s significantly improves the crystalline quality of films showing a preferential 0002 orientation even at a substrate temperature of 200 °C. This points to the importance of considering the kinetic effects of plasma-film interactions and their relevance for crystallite formation as well as influence on the composition of the films.

In a nutshell, this work presents effective mechanisms for producing PE-ALD AlN thin films with preferential c-axis orientation on 200 mm wafers, highlighting the importance of plasma source and parameter choice, as well as showing application potentials for growing layer stacks of ALD and sputtered layers without vacuum break in-between deposition.

4:45pm **AF2-TuA-14 Plasma-Enhanced Atomic Layer Deposition of High-Quality InN Thin Films Using a Novel In Precursor and NH_3 Plasma***, **Yejun Kim**, Chaehyun Park, Minjeong Kweon, Soo-Hyun Kim,* Ulsan National Institute of Science & Technology, Republic of Korea

Indium nitride (InN), a III-V nitride semiconductor, has a narrow bandgap (0.7 eV), high electron saturation velocity (4.2×10^{7} cm/s), low electron effective mass (0.07 m_0), and high electron mobility (4400 cm^2/V·s). These properties make InN ideal for sensors, optoelectronics, and high-electron-mobility transistors (HEMTs). However, MOVPE and MBE face challenges due to InN's low thermal stability (~ 500 °C decomposition into In and N_2), making them unsuitable for high-aspect-ratio microelectronics. Plasma-enhanced ALD (PE-ALD) enables precise thickness control and low-temperature processing, offering an alternative, though ALD-grown InN research is still in early stages. This study explores InN ALD using a novel ethanimidamidinate-based indium precursor and NH_3 plasma in a showerhead-type PE-ALD reactor (IOV dX1 PEALD, ISAC Research, Korea). The optimal deposition temperature was 275 °C, confirming self-limiting growth with a saturated rate of ~ 0.57 Å/cycle. A linear relationship between thickness and ALD cycles was observed. Film properties were analyzed using a 4-point probe (resistivity), SEM/TEM (thickness, step coverage), XRR (density, roughness), XRD (crystallinity), RBS (In/N ratio, impurities), UV-Vis (optical bandgap), and Hall measurement (carrier density, mobility). Detailed results will be presented at the conference.

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5:00pm **AF2-TuA-15 Insights Into Tuning TiO_2 Film Property Distribution in 3D Structures During Peald Process***, **Takashi Hamano**, Nobuyuki Kuboi, Hiroyasu Matsugai, Shoji Kobayashi, Yoshiya Hagimoto, Hayato Iwamoto,* Sony Semiconductor Solutions Corporation, Japan

Plasma-based deposition techniques are widely employed to fabricate cutting-edge electronic devices with vertical and complicated 3D structures. In addition, owing to the increasing demand for various advanced devices with organic films, low temperature deposition processes are required. During deposition processes, precise control of feature profile, i.e., coverage, and film properties is significant. In general, it is difficult to directly measure the film properties in a local area of 3D structures. Therefore, simulation techniques are effective tools to understand the deposition mechanisms in complicated 3D structures. Recently, we have developed a new simulation model based on the statistical ensemble method to predict both coverage and film properties and analyzed the PECVD and PEALD processes [1][2]. In this paper, we improved the simulation model and investigated the TiO_2 film properties in 3D structures during PEALD process.

In the simulation model, gas transportation and surface reactions, such as adhesion/desorption, migration, and binding are expressed by the movement of voxels using a stochastic algorithm. The voxel status indicating the bonding states and crystallinity is determined depending on the total energy flux of ions at each surface voxel solving the ion transportation in 3D structures. The variation in film thickness by ion bombardment is also modeled. The difference in the bonding states and crystallinity of TiO_2 between the planar region and sidewall of the hole structure was predicted. Especially, at lower process temperature, the film property distribution inside the hole structures becomes remarkable reflecting the distribution of incident ions.

To confirm the simulation results, we evaluated TiO_2 film properties inside the hole structures with an aspect ratio of 5 focusing on the wet etching rate (WER) of TiO_2. WER at the sidewall and bottom regions is several times higher than that at the planar region. In addition, the distribution of WER inside the hole structure notably changes depending on the process temperature.

Present results indicate that the process optimization considering both process temperature and ion irradiation (i.e., flux, energy and angular distribution of ions) is key to obtain the desirable film property distribution in 3D structures.

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5:15pm **AF2-TuA-16 The Application of Diiodosilane to Deposit SiN Film as Insulation Layer***, **YUN-CHIH Chiang**, Yong-Jay Lee,* Industrial Technology Research Institute, Taiwan

As chip miniaturization advances, the demand for thinner and more uniform films has increased. SiO_2 oxide films tend to emerge leakage current issues under this trend, whereas SiN films offer lower leakage current characteristics, gradually replacing SiO_2 as the insulating layer in MOSFETs. Traditional silicon-based precursors, such as silane or HCDS, perform well in mature process nodes like 20 nm. However, at smaller process nodes, these precursors lead to poor film quality. Switching to a precursor with higher reactivity, such as Diiodosilane (DIS), can improve film characteristics. Due to the lower bond energy of the Si–I bond, DIS enables film deposition at lower process temperatures, resulting in higher-quality SiN films while minimizing unreacted halogen residues. Additionally, DIS contains no carbon and can prevent carbon contamination in the deposited film, while releases less CO_2 during ALD process. These advantages make DIS a promising candidate for the usage of next-generation semiconductor processes below 3 nm.

In this study, DIS was used as an ALD precursor to deposit SiN films via plasma-enhanced atomic layer deposition (PEALD). In addition to demonstrate the advantages of DIS, we verified the SiN film which deposit by ALD process through ellipsometry, TEM, XPS, and electrical measurements. Furthermore, optimized process conditions were explored to achieve high-quality films, making this approach highly promising for advanced semiconductor devices in sub-3 nm processes.

ALD Fundamentals

Room Tamna Hall B - Session AF-WeM

Material Growth I

Moderators: Kivin Im, SK Hynix, **Gregory N. Parsons**, North Carolina State University

10:45am **AF-WeM-12 High Crystallinity Yttrium-Doped ZrO2 under 2 nm Through Atomic Layer Modulation***, **Ngoc Le Trinh**, Bonwook Gu, Wonjoong Kim, Minhyeok Lee,* Incheon National University, Republic of Korea*; Byung-ha Kwak,* Ajou University, Republic of Korea*; Hyun-Mi Kim, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea*; Youngho Kang,* Incheon National University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea*; Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

The rapid miniaturization of integrated circuits poses significant challenges for various silicon-based devices, such as DRAM capacitors and 3D transistors, which demand both high capacitance density and low leakage current density. As the device dimensions shrink further, the thin films used in these devices must become even thinner, making it increasingly difficult to preserve their physical properties at such reduced thicknesses. In this work, we studied high crystallinity dielectric thin films with Y-doped ZrO_2 (YZO) less than 2 nm of film thickness. Atomic layer modulation (ALM) based on atomic layer deposition (ALD) was utilized to achieve better compositional uniformity both in-plane and out-of-plane direction at atomic level. In the ALM process, the surface was sequentially exposed to precursors with an intervening purging step between each exposure, followed by a reaction with a counter-reactant, resulting in the growth of the YZO film within a single atomic layer. The ratio of Y and Zr in ALM film was determined by steric hindrance and chemical reactivity of the precursors. To design and interpret the experiment, two theoretical approaches, density functional theory (DFT) and Monte Carlo (MC) simulation were used. The formation energy of the crystalline phase in the ALM films was expected to be lower than in the ALD film. In the ALM film, Y atoms are formed closer to Zr atoms, with Y−O−Zr bonds forming both laterally and vertically within a few atomic layers. Consequently, the ALM film requires a lower energy barrier for diffusion to form theYZO crystalline phase, which enhances film density and improves crystallinity. It was revealed that doping ZrO_2 with Y induces a crystal structure change, leading to a phase transformation from monoclinic to a cubic (111)-plane-dominant phase. Consequently, YZO prepared via ALM shows approximately 250 times lower leakage current density compared to conventional YZO fabricated through ALD at a thickness of 2 nm. This key finding highlights that that YZO achieves both increased dielectric constant and reduced leakage current density at low thicknesses, demonstrating its potential as a promising material for future silicon device applications.

11:00am **AF-WeM-13 ALD Outstanding Presentation Award Finalist: Ultrahigh Purity Plasma-Enhanced Atomic Layer Deposition and Electrical Properties of Epitaxial Scandium Nitride***, **Bruce Rayner**, Noel O'Toole,* Kurt J. Lesker Company*; Bangzhi Liu, Jeffrey Shallenberger,* The Pennsylvania State University*; Jiadi Zhu, Tomas Palacios, Piush Behera, Suraj Cheema,* Massachusetts Institute of Technology*; Blaine Johs,* Film Sense*; Nicholas Strnad,* DEVCOM Army Research Laboratory

Scandium nitride (ScN) by plasma-enhanced atomic layer deposition (PEALD) was demonstrated on silicon (100), sapphire (0001) and magnesium oxide (001) substrates under ultrahigh purity conditions using a new Sc precursor, bis(ethylcyclopentadienyl)scandium-chloride [$ClSc(EtCp)_2$]. Out-of-plane x-ray diffraction patterns indicated single-crystal, cubic phase ScN deposited at 215°C on sapphire (0001) and magnesium oxide (001) substrates; phi-scans confirmed epitaxial growth. The ScN thin films grown on silicon with native oxide were polycrystalline with no preferential orientation. The ScN films showed a nitrogen-to-scandium ratio of approximately 1:1 measured by x-ray photoelectron spectroscopy, with ultra low levels of elemental impurities including 2.5 at.% chlorine, 0.9 at.% carbon and 0.4 at.% oxygen. $ClSc(EtCp)_2$ and N_2-H_2 plasma were evaluated as a ScN co-precursors at substrate temperatures ranging from 200-300°C, where we identified an ALD window between 200–215°C. Images by field emission scanning electron microscopy (FESEM) on 43 nm-thick films grown on untreated silicon revealed columnar grains with lateral sizes ranging from 16-28 nm. ScN conformality across 4:1 aspect ratio silicon trench structures with 312 nm-wide openings was also imaged by FESEM showing a top-to-bottom thickness ratio of 75%. ScN electrical properties were evaluated by performing Hall measurements to determine mobility, free electron concentration and resistivity. For ScN PEALD on magnesium oxide (001), the average mobility was 298 cm^2/Vs with a carrier concentration of 2.35×10^{19} cm^{-3}. The average resistivity was 1.01 mΩ·cm.

11:15am **AF-WeM-14 Microwave Enhanced (ME) ALD of HfO_2***, Jessica Haglund-Peterson, **John Conley**,* Oregon State University

The low temperatures typical of ALD can allow incorporation of impurities from unreacted ligands leading to sub-optimal physical, optical, and electrical properties. Although post deposition annealing (PDA) can help drive off impurities, the temperatures required may exceed thermal budget limits. To maintain low temperature while maximizing film properties, adding energy in-situ *during* each ALD cycle (energy enhanced, EE-ALD) can help drive/speed reactions and reduce impurity incorporation. Indeed, in-situ every cycle rapid thermal annealing improved the density, stoichiometry, electrical, and optical properties of ALD films that could not be achieved by PDA alone.[1-3] Other EE-ALD methods include flash lamp, plasma, UV, laser, and electron beam exposure.[4-9] It has been shown that *post*-deposition microwave annealing (MWA) can improve ALD films,[10] and recently, we introduced *in-situ* microwave enhanced (MWE) ALD.[11] Here we investigate low temperature MWE-ALD of HfO_2.

A Picosun R200 was equipped with a custom MW antenna (MKS) and an MKS SG 1024 solid state MW generator. HfO_2 was deposited at 150˚C using 1/30/0.1/30 sec TEMA-Hf/N_2/H_2O/N_2 ALD cycles. Film thickness and refractive index were modeled using a Film Sense FS-1 mapping ellipsometer. As compared to a control sample without MW exposure, adding 30 s in-situ 400 W MW exposures (*without* plasma generation) during the H_2O purges of each ALD cycle had no significant impact on growth. However, the same MW exposures during the TEMA-Hf purge were found to increase film thickness by ~50% and increase refractive index from 1.9 to 2.1 over the control sample. The impact during the precursor purge as opposed to H_2O purge is consistent with our previous results on TMA/H_2O Al_2O_3.[11] This work demonstrates quality ALD deposition at a temperature normally below the standard "window" for this process, allowing for a decrease in thermal budget. Additional electrical and analytical data will be presented, including density, crystallinity, stoichiometry, roughness, as well as leakage and capacitance of MOS and MIM device structures.

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11:30am **AF-WeM-15 Atomic Level Engineering of Dy-doped HfO2 Ultra-thin Films via Controlling Lateral and Vertical Mixing***, **Byung-Ha Kwak**,* Ajou University, Republic of Korea*; Ngoc Le Trinh,* Incheon National University, Viet Nam*; Bonwook Gu, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea

We investigate the effects of Dy doping in HfO_2 thin films using two distinct atomic arrangement strategies: lateral mixing, known as atomic layer modulation (ALM), and vertical mixing, known as supercycle ALD. Lateral mixing can control atomic concentration by sequentially exposing two precursors (Dy and Hf) in a first-half cycle of ALD process and exposing a single reactant that reacts both precursors at the second-half cycle, determined by chemical reactivity and steric hindrance of two precursors.[1] This method allows precise controlling of atomic-level doping even in ultrathin films under 5 nm thickness. In contrast, the vertical mixing method, where a few cycles of Dy_2O_3 deposition are followed by multiple cycles of HfO_2, has limitations[2], as it requires a minimum thickness to maintain a consistent concentration across the film.

In the lateral mixing process, when both precursors were sequentially exposed for their respective saturation times, the Dy concentration in deposited films was measured to be 20.6 % when a Dy precursor was exposed first, whereas it was 12.5 % when a Hf precursor was exposed first. We elucidate growth mechanism of ultra-thin films of lateral mixing by density functional theory (DFT) and Monte-Carlo (MC) simulations with experimental observation. We observe different crystalline structures between lateral mixing and vertical mixing. In single HfO_2 and vertical mixing films, tetragonal (101) phase was observed after 600 ℃ annealing process. However, no crystalline phase was observed in lateral mixing films at the same annealing process. We also observe that both lateral mixing and vertical mixing films showed lower leakage current density than a single HfO_2 film of same thickness, which will be discussed with growth mechanism and crystalline structure. Interestingly, the lateral mixing case for Hf-precursor-exposed first exhibits leakage currents approximately 180 times lower than Dy-precursor-exposed first. We believe that these approaches will significantly advance the development of high-k materials with optimized properties, supporting the future scaling down of semiconductor devices and enhancing their performance in next-generation electronic applications.

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11:45am **AF-WeM-16 Process-Structure-Properties of Atomic Layer Deposited Niobium Nitride and Evolution of Strain with Plasma Chemistry**, ***Neeraj Nepal***, *Joseph C Prestigiacomo, Maria Gabriela Sales, Peter M Litwin, Vikrant J Gokhale, Virginia D Wheeler,* U.S. Naval Research Laboratory

Niobium nitride (NbN) has exceptional physical, chemical, and electrical properties that can be utilized in a range of applications such as gate metal, superconducting qubits and detectors (T_c ~9-17 K [1]), RF antennas, resonators, and Cu interconnect diffusion barriers. For all these applications, a low temperature growth process with wafer scale uniformity, conformality, and subatomic thickness control is highly desirable. Atomic layer deposition (ALD) provides a path towards integration of NbN at lower temperatures with control over the desired properties. Most reported thin plasma-enhanced ALD (PEALD) NbN films [2-3] to date are either amorphous or polycrystalline. In this talk, we report on highly oriented single phase, PEALD NbN (111) films and discuss the evolution of strain with plasma chemistry.

ALD NbN films were deposited on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor using (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN) and N_2/H_2 plasma precursors. Similar to previous reports [2], TBTDEN required a boost to enable growth. Growth windows and film morphological, structural, and electrical properties were optimized for TBTDEN temperature (80-100°C), TBTDEN boost (1-2s), TBTDEN pulse (1.5-2.0s), plasma pulse (20-30s), H_2/N_2 ratio (1.5-12.5), and temperature (150-400 °C). Optimum growth parameters (TBTDEN = 100°C, TBTDEN boost = 1.5s, TBTDEN pulse = 2s, and H_2/N_2 = 60/20sccm) yielded an ALD window from 250-300°C with a growth rate (GR) of ~ 0.5A/cy. While GR was almost constant for $N_2 \geq 20$ sccm, room temperature resistivity (ρ_{RT}) increased linearly with N_2 flow. High-resolution XRD scans show 1st and 2nd order (111) NbN peaks. Lattice constants obtained from XRD show that strain changes from compressive to tensile with increasing N_2 flow, in which an N_2 flow of 20 sccm provided an almost strain-free film. The compressively strained 12.6 nm thick film at 5 sccm N_2 resulted in lower ρ_{RT} (~139μΩcm) and superconducting critical temperature (T_c~12.26K). Measured T_c is similar or higher than reported T_c (12.10K) of 15nm thick ALD NbN films [3]. For an optimized 30nm thick film, carbon is below the XPS detection limit, RMS surface roughness is 0.52nm, and rocking curve FWHM is 0.69°, which is narrower than previously reported for 30 nm thick films [3]. T_c on all those films were also measured to establish process-structure-property relationships, and results will be discussed in the context of use in quantum and high temperature contact applications.

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ALD Fundamentals
Room Tamna Hall B - Session AF-WeA

Material Growth II

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, **Erwin Kessels**, Eindhoven University of Technology, Netherlands

1:30pm **AF-WeA-1 ALD of Nitride Semiconductors***, **Henrik Pedersen,*** Linköping University, Sweden **INVITED**

The group 13 nitrides, AlN, GaN, InN and their alloys, is an important class of semiconductors, forming the backbone for technologies such as light emitting diodes (LEDs) and high electron mobility transistors (HEMTs). Chemical vapor deposition (CVD) at high temperatures, 800-1200 °C, is the typical way of depositing these materials. But CVD of indium nitride (InN) is severely limited by the low thermal stability of the material,[1] and can thus only tolerate relatively low deposition temperature. As ALD is intrinsically low temperature, it is a logical path for InN films and has been demonstrated to deposit epitaxial InN films with excellent crystalline quality.[2,3] The two chemically and structurally closely related materials aluminium nitride (AlN) and gallium nitride (GaN) has been deposited by both plasma and thermal ALD, with ammonia (NH_3) as nitrogen precursor in thermal processes.

In this talk I will describe ALD of these semiconducting nitrides, with focus on the fundamental understanding of the ALD chemistry. ALD has been shown to be an enabler for the metastable InN and $In_xGa_{1-x}N$ with x close to 0.5.[4] By combining quantum-chemical density functional theory (DFT) calculations[5] and *in-situ* techniques such as mass spectroscopy[6], we can present a detailed surface chemical model for the ALD processes. I will also present results from our efforts understand the surface chemistry by *in operando* ambient pressure XPS. Finally, I will discuss limitations to thermal ALD of these nitrides and why plasma activation seems to be needed.

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2:00pm **AF-WeA-3 Towards Two New Atomic Layer Deposition Processes for the Distinct Synthesis of Coo or Co_3O_4 Thin Films***, **Olivier Debieu,*** CIRIMAT, Université de Toulouse (CNRS / INP / UT3), Ensiacet, France*; Getaneh Diress Gesesse, Julien Cardin, Bilal Bawab, Christophe Labbe, Cédric Frilay, Sylvain Duprey,* CIMAP, ENSICAEN, UNICAEN, CEA, CNRS UMR5262, France*; Jean-François Lohier,* CRISMAT, ENSICAEN, UNICAEN, CNRS UMR6508, France

Rock salt CoO and spinel Co_3O_4 are two p-type semiconductors (SCs) with a wide range of promising applications, used alone or assembled with other n-type SCs as active material in gas sensors, or as electrode in photoelectrocatalysis (PEC) as in the present project [1,2]. Based on the application conditions, *i.e.* the (photo)electrochemical conditions, metastable CoO thin films with the lowest Co^{2+} oxidation state can be more suitable than the most stable Co_3O_4 with Co^{3+} and Co^{2+}·oxidation states. Depending on the growth method, the two phases are not necessarily achievable or may coexist at the nanograins scale. Atomic layer deposition (ALD is a versatile deposition technique that allows fine control of the composition, crystalline structure and morphology of conform layers, making it then highly suitable for the targeted applications.

The present study focuses on the optimization of two new ALD recipes and annealing conditions by the substrate temperature, gas flows, and oxidizing reactant and proper annealing atmosphere to synthesis either CoO or Co_3O_4 films on Si wafer using CoAMD as precursor. To establish the relationships between these parameters and the structural and optical properties of the films, GI-XRD, XRR, FTIR, UV-Vis-NIR, and ellipsometry (SE) analysis were used. We found comparable thicknesses by XRR and by SE that were useful to select the best growth rate conditions. Comparable crystallographic compositions revealed by GI-XRD and FTIR were found to change with the ALD parameters. Interestingly, the normal incidence in FTIR measurement can act as a filter to analyze only Co_3O_4 IR-features. We found optical dispersion curves of CoO and Co_3O_4 layers, rare in the literature, modeled by standard critical point models, and 6-Lorentzian models corresponding to the six optical transitions in the 0.5-5 eV spectral range of SE measurements, respectively, providing information on the density. Two optimal synthesis routes have been thus developed at lowest thermal budget.

Following the successful synthesis of the two Co-oxide allotropes, we will assemble them on our previously prepared Nb-doped TiO_2 films[3] to form a p-n photoelectrodes (in oxidation or reduction conditions). Electrical characterizations at nanoscale using conductive AFM[4] will be performed to assess carrier transport properties before PEC activity measurement.

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2:15pm **AF-WeA-4 High-Quality ALD-Ru Process Using Thermally Stable ALD Ru Precursor***, **Hideaki Nakatsubo,*** TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd. / UNIST, Japan*; Jeongha Kim, Soo-Hyun Kim,* UNIST, Korea (Democratic People's Republic of)

Ruthenium (Ru) is expected to be a promising alternative material for copper (Cu), due its better scaling performance resulting from a shorter electron mean free path and possibility of the barrierless interconnectes scheme. Until now, many atomic layer deposition (ALD) processes have been developed to achieve a high-quality Ru film with a low resistivity as possible (bulk resistivity of Ru: 7.4 μΩ·cm), but many reported values have not yet achieved the desired low resistivity one. In this study, a novel Ru precursor, trimethylenemethane (p-methylisopropyl benzene) ruthenium [Ru(TMM)(p-cymene)], was synthesized and investigated for a high-quality ALD-Ru process. Since this precursor has a thermal stability up to 400 ℃, one can adopt a high process temperature for ALD, giving a lower resistivity than those obtained many previous ALD processes typically performed lower than 300 ℃ due to the poor thermal stability of Ru precursors. For developing ALD-Ru process, O2 was used as a reactant, and substrates used included SiO2, TiN, and Ru. The ALD-Ru process nicely shows a typical self-limiting behavior of ideal ALD with a growth per cycle (GPC) of ~1.28Åon TiN and a negligible incubation cycle at the deposition temperature of 300 oC. Interestingly, on SiO2, there was no Ru deposition even after 1000 cycles. The resistivity decreased with increasing process temperature, reaching ~14 μΩ·cm at 300℃ and ~11 μΩ·cm at 375℃, comparatively lower than those of previously reported Ru ALD processes. Annealing the Ru film in H2 gas further reduced resistivity to 8.65 μΩ·cm at 700℃, close to the bulk Ru resistivity. XRD and SEM analysis showed increased grains size and improved crystallinity with annealing, resulting in the decrease in the resistivity. In conclusion, the present study demonstrates high-performance and versatile ALD-Ru process with a very low resistivity, high GPC, and extremely high selectivity can be achieved using a newly synthesized Ru precursor.

2:30pm **AF-WeA-5 The Development of Ultralow-Dielectric Constant Boron Nitride Film by Novel Plasma Atomic Layer Deposition***, **Kazuki Goto,** Yoshihiro Kato, Shuichiro Sakai, Hiroki Murakami, Yamato Tonegawa,* Tokyo Electron Technology Solutions Ltd, Japan

The miniaturization of electronic devices has intensified challenges related to electrical signal propagation delays, primarily due to increased wiring resistance and capacitance. As a response, there is a rising demand for low dielectric constant (low k) materials to enhance device performance. Silicon oxide-based dielectrics (SiCOH) are conventionally known as a low k material. However, the thermal and mechanical stability of these materials are significantly compromised due to their low film density. In this context, boron nitride (BN) films have emerged as promising candidates due to their low dielectric constant and high stability [1]. Hexagonal BN (*h*BN) is characterized by its layered structure and wide band gap (5.2 – 5.9 eV), and it is expected to exhibit low k values, particularly along the c-axis [2].

In this study, we explored the film formation process of *h*BN using a borazine-based precursor with N_2 and NH_3 plasma to achieve high-quality BN films with low k, high density, and high conformality. Deposition was conducted at 400 ℃ on a 300 mm Si substrate, resulting in an ideal *h*BN layered structure clearly revealed by cross-section TEM (Fig. 1a). It was possible to deposit even thicker layers while maintaining the *h*BN structure. Moreover, we have successfully deposited conformal *h*BN on a trench pattern for the first time (Fig. 1b), expanding the applicability and versatility of *h*BN. C-V measurements indicated a low k value of <3 for our *h*BN. Analysis through XPS and IR spectroscopy confirmed a stoichiometric BN composition containing a significant amount of B-N sp^2 bonds. By applying additional plasma treatments, we observed a reduction in k value along with increased density due to the promotion of sp^2 B-N bonding. The resulting *h*BN films exhibited a low k value at higher density than can be achieved with Si-based films (Fig. 2).

This methodology also facilitated control over the crystalline orientation of *h*BN. We found certain processing conditions led to the deposition of both less and highly ordered *h*BN. C-V measurements across varying oriented films demonstrated a decrease in k values correlating with order, while I-V measurements confirmed that order in crystallinity contributed to the reduction of leakage current. We established a relationship between the crystallinity of *h*BN, the k value, and leakage current. This research created high quality conformal *h*BN, demonstrating significant potential for practical applications as low dielectric constant films for high-performance semiconductor devices.

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2:45pm **AF-WeA-6 Thermal Atomic Layer Deposition of InN using Hot-wire-activated NH_3 and Hydrazine Reactants***, **Bonwook Gu**, Kwangyong An, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

Indium nitride (InN) possesses high electron mobility, approximately 3000–4000 $cm^2/V{\cdot}s$) and a low bandgap (~0.7 eV), making it an ideal material for high-speed transistors and RF devices that require low-power, high-performance operation. Additionally, InN exhibits excellent infrared absorption properties, enabling its applications in infrared detectors, high-efficiency solar cells, and optical sensors. Recently, as device sizes have decreased and structures become more complex, research on atomic layer deposition (ALD) for fabricating InN thin films has gained significant momentum. However, previous InN ALD research has primarily focused on plasma-enhanced processes, which pose challenges such as (1) difficulty in achieving uniform film deposition on three-dimensional structures with high aspect ratios and (2) potential substrate damage due to high-energy plasma exposure. To address these limitations, we explored the feasibility of thermal ALD for InN deposition. Thermal ALD for InN is challenging due to the high deposition temperatures required, low reactivity of reactants, and the tendency of indium compounds to oxidize easily, leading to poor film quality and low deposition efficiency. In this research, we employed hydrazine and hot-wire-activated NH_3 as reactants for thermal InN ALD. We conducted a comparative study using trimethylindium (TMI) and InPALA as In precursors. The physical and chemical properties of the deposited InN thin films were characterized using X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

3:00pm **AF-WeA-7 Electron-Enhanced ALD and CVD of Titanium-, Silicon- and Tungsten-Containing Films at Low Temperatures Using Metal Precursors with Various Reactive Background Gases***, Zachary C. Sobell, **Andrew S. Cavanagh**, Steven M. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) (Figure 1a) and electron-enhanced chemical vapor deposition (EE-CVD) (Figure 1b) can be employed for the low temperature deposition of thin films using metal precursors with various reactive background gases (RBGs).EE-CVD expands on the previous report of TiN EE-ALD using alternating $Ti(N(CH_3)_2)_4$ (tetrakisdimethylamino titanium (TDMAT)) and electron beam exposures with NH_3 RBG.During EE-CVD, the electron beam and the RBG are present continuously.Together with the RBG and electron beam incident on the surface, the metal precursor is pulsed into the vacuum chamber to control the film growth.

In this work, the metal precursors were TDMAT, Si_2H_6, and $W(CO)_6$.The RBGs were O_2, NH_3, CH_4, and H_2.The studies demonstrated TiO_2 EE-ALD and SiN, SiO_2, SiC_x, Si, W_2N, WO_3, and WC_x EE-CVD. To illustrate EE-ALD, TiO_2 EE-ALD was performed at T < 80 °C using alternating TDMAT and electron beam exposures together with O_2 RBG.The growth rate for the TiO_2 EE-ALD was ~0.7 Å/cycle.The TiO_2 EE-ALD films were nearly stoichiometric, displayed crystallinity, and were smooth as measured by atomic force microscopy (AFM).

To illustrate EE-CVD, SiC_x EE-CVD was performed at T < 100 °C using repeating Si_2H_6 pulses with continuous electron beam and CH_4 RBG exposures.XPS revealed a 1:1 Si:C stoichiometry for a CH_4 RBG pressure of 0.45 mTorr and C-rich films for higher CH_4 RBG pressures.The SiC EE-ALD growth rate was ~0.4 Å per Si_2H_6 pulse.The stoichiometric SiC EE-CVD films were smooth as measured by AFM.

W_2N EE-CVD was also performed at T < 120 °C using repeating $W(CO)_6$ pulses with continuous electron beam and NH_3 RBG exposures (Figure 2a).The W_2N EE-CVD growth rate was ~0.17 Å per $W(CO)_6$ pulse.The W_2N films had a resistivity of ~450 μΩ-cm.The W_2N EE-CVD films also displayed crystallinity and high purity (Figure 2b).This work shows that EE-ALD and EE-CVD with various RBGs can deposit a broad range of materials at low temperatures including oxides, nitrides and carbides.

3:15pm **AF-WeA-8 Low-Temperature Atomic Layer Deposition of (00l)-Oriented Elemental Bismuth***, **Amin Bahrami**, Jorge Luis Vazquez-Arce, Alessio Amoroso, Nicolas Perez,* Leibniz Institute for Solid State and Materials Research, Germany*; Jaroslav Charvot,* University of Pardubice, Czechia*; Dominik Naglav-Hansen,* Ruhr-University Bochum, Germany*; Panpan Zhao, Jun Yang, Sebastian Lehmann, Angelika Wrzesińska-Lashkova,* Leibniz Institute for Solid State and Materials Research, Germany*; Fabian Pieck, Ralf Tonner-Zech,* Leipzig University, Germany*; Filip Bureš,* University of Pardubice, Czechia*; Annalisa Acquesta,* University of Napoli Federico II, Italy*; Yana Vaynzof, Anjana Devi, Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

This study presents the first successful demonstration of growing elemental bismuth (Bi) thin films via thermal atomic layer deposition (ALD) using Bi(NMe2)3 as the precursor and Sb(SiMe3)3 as the co-reactant. The films were deposited at a relatively low temperature of 100 °C, with a growth per cycle (GPC) of 0.31-0.34 Å/cycle. Island formation marked the initial growth stages, with surface coverage reaching around 80% after 1000 cycles and full coverage between 2000 and 2500 cycles. Morphological analysis revealed that the Bi grains expanded and became more defined as the number of ALD cycles increased. This coalescence is further supported by X-ray diffraction (XRD) patterns, which show a preferential shift in growth orientation from the (012) plane to the (003) plane as the film thickness increases. X-ray photoemission spectroscopy (XPS) confirmed the presence of metallic Bi with minimal surface oxidation. Temperature-dependent sheet resistance measurements highlight the semimetallic nature of Bi, with a room temperature resistivity of ≈200 μΩcm for the 2500 cycles Bi. Temperature-dependent sheet resistance was also associated with a transition in carrier-type dominance from electrons at higher temperatures to holes at lower temperatures.

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