Thin Films Division
Room 102A - Session TF1-MoM
Precursors and Surface Reactions

Moderators: Cathleen Crudden, Queen's University, Canada, Markku Leskela, University of Helsinki, Finland

8:20am **TF1-MoM-1 Monitoring the Transient Surface Species during TiO_2 Atomic Layer Deposition using Surface-Enhanced Raman Spectroscopy***, **Ryan Hackler**[1], G Kang, G Schatz, P Stair, R Van Duyne,* Northwestern University

It is important to understand the dynamic surface chemistry that takes place during various atomic layer depositions (ALD) if high quality thin films with well-defined physical characteristics are to be achieved. In this work, ALD of TiO_2 was performed in tandem with *in-situ* surface-enhanced Raman spectroscopy (SERS) to monitor changes in the transient surface species present and to determine whether changes in the surface chemistry dramatically affect growth rate and purity. To ensure nucleation of the titanium precursor took place close enough to the plasmonic substrate necessary for SERS, a self-assembled monolayer of 3-mercaptopropionic acid (MPA) was used as a capture agent, with titanium tetraisopropoxide (TTIP) as the titanium precursor. Comparisons between the Raman spectra of the neat precursor and the SER spectra of the first ALD cycle of TiO_2 reveal typical ligand exchange chemistry, with self-limiting behavior and intact isopropoxide ligands. Subsequent cycles of TiO_2 ALD, however, show drastically different chemistry. No common vibrational modes between the neat precursor and the surface species are found in subsequent cycles, suggesting a lack of isopropoxide ligands. Continuous exposure of either TTIP or isopropanol after the 1st ALD cycle also results in atypical product formation coupled with unlimited CVD-like growth. Comparisons with alternative precursors (aluminum isopropoxide and titanium *tert*-butoxide) and DFT calculations reveal the isolated TiO_2 sites from the 1st ALD cycle play a role in the dehydration of isopropoxide ligands from subsequent TTIP doses. The resulting propene then undergoes oxidation with the help of the underlying plasmonic silver substrate before polymerizing into indistinguishable carbon products that accumulate on the surface. The observed dehydration chemistry is expected to be the result of the initial TiO_2 sites and is thus believed to be inherent when using TTIP as a precursor for TiO_2 ALD. As a result, considerations must be made regarding the viability of a surface for TiO_2 ALD using TTIP that were previously overlooked, such as reactivity to propene.

8:40am **TF1-MoM-2 Theoretical Study on the Effect of Precursor Ligand in Atomic Layer Deposition of Al_2O_3 on SiO_2***, **Tania Sandoval,*** Universidad Técnica Federico Santa María*; T Liu,* Stanford University*; R Tonner,* Philipps-Universität Marburg*; S Bent,* Stanford University

Atomic layer deposition (ALD) relies on the adsorption of metalorganic and inorganic molecules to create thin and conformal films for semiconductor device fabrication. Aluminum precursors, particularly trimethylaluminum (TMA), have been used for decades to deposit thin dielectric films. The reaction mechanism for this process is well known and reported in literature. However, with continued advances in semiconductor nanofabrication and thin film deposition, the ability to select precursors that meet different processing requirements is important. For this purpose, it is necessary to fundamentally understand the effect that the precursor structure can have on nucleation and growth. Thus, in this work, the adsorption of a series of Al-X molecules ($X= –CH_3$, $–Cl$, $–C_2H_5$, and $–C_3H_8$) on SiO_2 were explored. In the series, TMA is used as a model system and benchmark for comparison.

Density functional theory (DFT) calculations suggest interesting trends regarding the adsorption of Al-X molecules on SiO_2. Results indicate that when the number of Cl ligands on Al is increased, the dative bond that forms between the precursor molecule and the SiO_2 surface becomes more exothermic with respect to TMA. This increase is a result of electronic contributions to the total energy, which can be attributed to inductive effects caused by the addition of the Cl ligand. Additionally, it is observed that increasing the number of carbon atoms in an alkyl ligand stabilizes the dative bond; however, these surface adducts are primarily stabilized by dispersion interactions, which could be related to the ligand size. After initial adsorption of Al-X, either the alkyl or chorine ligand exchange reaction can proceed. Our DFT results suggest that exchange of the alkyl ligand is more thermodynamically favorable than that of the Cl ligand, which correlates well with the higher dissociation energy observed for Al-Cl versus Al-C.

Preliminary X-ray photoelectron spectroscopy (XPS) results for ALD using dimethylaluminum chloride and aluminum trichloride as precursors show chlorine at the silicon surface, suggesting only a partial ligand exchange reaction. These experimental results agree with our theoretical findings which show Cl-ligand exchange to be less thermodynamically favorable than the precursor state (dative bond). These results provide interesting insights into both the fundamental aspects of the adsorption chemistry of organometallic compounds on semiconductor surfaces and the practical aspects of designing precursor molecules for ALD growth.

9:00am **TF1-MoM-3 Relevance of Dimeric and Tetrameric Structures to the Surface Chemistry of Metal Amidinate Atomic Layer Deposition Precursors***, **Bo Chen**, Y Yao, Q Ma, F Zaera,* University of California, Riverside*; Y Duan, A Teplyakov,* University of Delaware*; J Coyle, S Barry,* Carleton University

The search for appropriate metallorganic compounds with clean chemistry has long been one of the central issues in atomic layer deposition (ALD) development. Metal amidinates have been shown to be excellent candidates for such purpose owing to their relatively simple synthesis methodology, fair volatility and reactivity, and ease with which they can be modified at the ancillary peripheral moieties. Recent studies of these compounds have suggested that they tend to dimerize, and in some cases even form tetramers, in the solid state. This finding raises important questions regarding the structures of metal amidinates during their vaporization, dosing, and activated adsorption in ALD process. In our study, three families of copper amidinate precursors, copper(I)-*N*,*N'*-di-*sec*-butyl-acetamidinate, copper(I)-*N*-*sec*-butyl-2-iminopyrrolidinate, and copper(I)-*N*-*tert*-butyl-5,5-dimethyl-2-iminopyrrolidinate, have been investigated to test the role of steric effects in ligand substituents on their surface chemistry over nickel and silicon oxide surfaces. It has been found that, by following specific ligand design strategies such as strengthening inner C–N bonds and preventing *β*-hydride elimination, it is possible to improve on the thermal stability of these precursors, and consequently on the chemical quality of the deposited films. Liquid-injection field desorption ionization mass spectrometry data proved that the dimeric and tetrameric structures of the copper amidinates in the solid state are retained upon vaporization into the gas phase (the dimers for the first and third compounds, a tetramer for the second), and X-ray photoelectron spectroscopy data pointed to the retention of the dimeric structure on the surfaces. Density-functional theory calculations of the relative energies of formation of the monomers, dimers, and tetramers confirmed the experimental results. The retaining of dimeric and tetrameric structures of metal amidinates upon initial adsorption implies that the dissociation of the dimers into the monomers on solid surfaces, as required in ALD processes, is likely to occur at high temperatures, to induce Cu reduction and ligand decomposition.

9:20am **TF1-MoM-4 Low Temperature Dielectric ALD with the use of Hydrogen Peroxide: Comparison of Growth and Film Characteristics for Anhydrous H_2O_2, H_2O_2/H_2O Mixtures and H_2O***, **Daniel Alvarez**, K Andachi, J Spiegelman,* RASIRC

Novel precursor chemistries are being sought for ALD of dielectrics, where a tremendous amount of effort has been put into development of new Organometallic and Organosilicon precursors. Our approach focuses on providing a novel oxidant that may improve the reactivity of precursors that react slowly or incompletely with water. Our approach entails the development of two hydrogen peroxide gas delivery systems:

1. An ampoule based formulation for anhydrous hydrogen peroxide, where H_2O_2 is delivered in the gas phase in the absence of water by use of a membrane delivery system.
2. A gas generator approach, where a high concentration H_2O_2/H_2O mixture is delivered by in situ concentration methods and the use of a membrane vaporizer.

Anhydrous Hydrogen Peroxide Gas

Initial ALD results for growth of ZrO_2 from anhydrous H_2O_2 and $CpZr(N(CH_3)_2)_3$ show high quality film growth at 260C. A linear growth curve is observed with minimal saturation delay. ZrO_2composition was characterized by XPS and XRR, with results very similar to films grown with ozone. In addition, films resulting from H_2O_2 ALD were placed into MIMCAP

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[1] **National Student Award Finalist**

structures. These structures show high k values of 35, slightly improved over those grown with a 20% ozone concentration at 32.

High Concentration Hydrogen Peroxide Gas

A novel gas generator for delivery of H_2O_2/H_2Omixtures has been developed. This equipment utilizes a carrier gas and delivers up to 5% H_2O_2/21% H_2O gas by volume from 30wt% H_2O_2 liquid solution (H_2O/H_2O_2=4.2). This gas mixture enables lower-temperature growth processes vs water, where HfO_2 films may be grown at temperatures as low as 100C.

Our current focus is on low temperature growth of SiO_2 ALD. Reactions of tris(dimethylaminosilane) $(N(CH_3)_2)_3SiH$ were performed with H_2O_2. Film characterization for anhydrous H_2O_2, H_2O mixtures, and water will be compared for films growth at 300C. Wet etch rates and refractive index will also be reported. Applications for multiple pattern spacers and hardmasks will also be discussed.

9:40am **TF1-MoM-5 Putting More Chemistry into CVD. Precursors, Superconformality, and Selectivity***, **Gregory Girolami**, J Abelson,* University of Illinois at Urbana-Champaign **INVITED**

This talk will cover recent work on the synthesis of new CVD precursors for transition metals that combine air stability with good shelf life and high volatility, and studies of the mechanism by which they thermolyze. We will also describe our efforts over the last few years to develop new kinds of CVD methods that are able to deposit films both conformally and superconformally, as well as selectively on some surfaces but not on others. Our approach has been to think like chemists and to use kinetic concepts such as inhibition, differential diffusion, and rate laws to invent new methods to control film thickness as a function of depth. A variety of specific examples of our new approaches will be illustrated.

10:40am **TF1-MoM-8 Insight into the "Residual Methyls" during ALD of Al_2O_3 from TMA/H_2O using *in situ* RAIRS***, **Brent Sperling**, B Kalanyan, J Maslar,* National Institute of Sandards and Technology (NIST)

Despite being arguably the most well-studied and widely-used precursor pairing used for atomic layer deposition, trimethylaluminum (TMA) and H_2O continue to provide surprises. One of the most recent is the discovery that "residual" surface methyl groups persist at low temperatures even after large doses of H_2O, as observed using broadband sum-frequency generation (BB-SFG).[1] Our measurements using *in situ* reflection-absorption infrared spectroscopy (RAIRS) in a laminar-flow reactor have found evidence supporting the BB-SFG findings under typical ALD conditions. Post-deposition XPS measurements indicate that, in agreement with numerous other studies, very low concentrations of carbon are present in the resulting films even at low temperatures when residual methyls are present. With RAIRS, we observe a significant (approximately 10 cm^{-1}) reduction in the frequency of the deformation mode at ~1210 cm^{-1} after H_2O dosing. Small additions of H_2O allow the dynamics to be captured; as the intensity decreases and peak position changes, the peak shape remains constant. Explanations for the behavior are discussed along with suggestions on how this observation might be used to elucidate some the finer details of TMA/H_2O surface chemistry.

[1] V. Vandalon and W.M.M. Kessels, *Appl. Phys. Lett.***108**, 011607 (2016).

11:00am **TF1-MoM-9 Low Temperature Atomic Layer Deposition of Silicon Nitride using Hexachlorodisilane and Ultra-High Purity Hydrazine***, **Aswin Kondusamy**, A Lucero, S Hwang, X Meng, H Kim,* University of Texas at Dallas*; D Alvarez Jr., J Spiegelman,* RASIRC*; J Kim,* University of Texas at Dallas

Silicon nitride is an important material in the semiconductor industry for applications in 3D integration and self-aligned patterning. The conventional processes used to deposit silicon nitride involve either high temperature or plasma to generate reactive species. Though they can produce good quality films in terms of electrical properties, wet etch rate and uniformity [1], they do not satisfy the demands for modern applications namely low thermal budget (<400 °C) and conformality over high aspect ratio structures. Newly developed ultra-high purity hydrazine sources have been successfully used to deposit metal nitrides at low temperature.[2] In this work, we studied the growth and properties of silicon nitride films deposited by low temperature Atomic Layer deposition (ALD) using Hexachlododisilane (HCDS) and Hydrazine.

Silicon nitride films were deposited in the temperature range 250-400 °C. The growth per cycle (GPC) gradually increased with hydrazine exposure and saturation behavior was observed. GPC of 0.4-0.5 Å/cycle is observed at 400 °C with refractive index of 1.813. X-Ray Spectroscopy showed that films of low oxygen (<2%) and chlorine (<1%) impurity can be achieved. These results are similar to those for films deposited with HCDS and NH_3 using Plasma-enhanced ALD at 360°C. Film density and wet etch rate results are compared for films deposited at different temperatures.

1. X. Meng, Y.-C. Byun, H. Kim, J. Lee, A. T. Lucero, L. Cheng, J. Kim, *Materials* 9 (12) 1007 (2016)

2. D. Alvarez, J. Spiegelman, R. Holmes, K. Andachi, M. Raynor, H. Shimizu, *ECS Transactions*, 77 (5) 219-225 (2017)

11:20am **TF1-MoM-10 Investigating Low-Temperature Atomic Layer Deposition of Nickel Oxide using $Ni(^{tBu2}DAD)_2$ and Ozone***, **Konner Holden**, J Conley, Jr.,* Oregon State University*; C Dezelah,* EMD Performance Materials

Nickel oxide (NiO), a wide band gap p-type oxide semiconductor, is of interest for applications in solar energy conversion [1], electrocatalysis [2], and as a tunnel barrier for metal/insulator/metal (MIM) diodes for infrared energy harvesting. Atomic layer deposition (ALD) is an ideal technique for the highly conformal, uniform thin films needed for these applications. Herein, we develop a new process for ALD of NiO using $Ni(^{tBu2}DAD)_2$ and O_3-.

ALD growth of metallic Ni has been demonstrated recently using $Ni(^{tBu2}DAD)_2$ and *tert*-butylamine [3]. ALD of metallic cobalt [4] and cobalt oxide [5] have been reported using $Co(^{tBu2}DAD)_2$ with formic acid and O_3, respectively. Here, we report the use of $Ni(^{tBu2}DAD)_2$ and O_3 for ALD of NiO. NiO was deposited in a Picosun Sunale R-150 using N_2-purge-separated cycles of $Ni(^{tBu2}DAD)_2$ held at 140°C and an O_3/O_2 mixture of ~10%. NiO films were characterized using variable angle spectroscopic ellipsometry (VASE) and grazing-incidence x-ray diffraction (GIXRD).

A plot of thickness vs. temperature for depositions using 135 cycles of a 5/30/4/30 s $Ni(^{tBu2}DAD)_2/N_2/O_3/N_2$ pulse sequence shows slightly decreasing growth with increasing temperature in the range of 175°C to 225°C (Fig. 1). In this temperature range, the refractive index is roughly constant at 2.38, consistent with reports for bulk and thin film NiO. Below 175°C, growth increases more steeply, likely due to condensation. Above 225°C, growth continues to decrease, due to desorption or possibly upstream precursor decomposition. A more detailed investigation of growth per cycle (GPC) versus temperature is underway. At 200°C, a linear GPC is observed, and saturating growth is observed for O_3 pulses of 4 s and longer, using a 5/30/x/30 s sequence (Fig. 2), while softer saturation is observed for $Ni(^{tBu2}DAD)_2$ pulses of 1 s and longer using a x/30/4/30 s sequence and is under further investigation. A GIXRD scan of an ~18 nm thick film deposited at 200°C indicates polycrystalline cubic NiO (Fig. 3).

Atomic force microscopy (AFM), x-ray reflectivity (XRR) and x-ray photoelectron spectroscopy (XPS) characterizing surface morphology, density, and composition, respectively, will be discussed at the meeting as well as dielectric properties (leakage, breakdown strength, dielectric constant, etc.) revealed by metal/insulator/metal (MIM) test devices.

[1] S. Seo et al., Nanoscale 8, 11403 (2016).

[2] K. L. Nardi et al., Adv. Energy Mater. 5 (2015).

[3] M. M. Kerrigan et al., ACS Appl. Mat. & Interfaces. 10, 14200 (2018).

[4] J. P. Klesko, M. M. Kerrigan, and C. H. Winter, Chem. Mater. 28, 700 (2016).

[5] J. Kim et al., Chem. Mater. 29, 5796 (2017).

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