

ALD Fundamentals

Room Plaza F - Session AF-MoA

ALD Fundamentals: Characterization (1:30-3:30 pm)/Mechanisms and Surface Science (4:00-5:00 pm)

Moderators: Mikko Ritala, University of Helsinki, David Emslie, McMaster University, Simon Elliott, Tyndall National Institute, University College Cork

1:30pm **AF-MoA-1 FTIR and NMR Analysis of ALD Al₂O₃ on poly-L-lactone Acid Powder and Electrospun Fibres**, *Laura Svärd, T Virtanen, M Putkonen, E Kenttö, H Rautkoski, P Heikkilä, P Simell*, VTT Technical Research Centre of Finland, Finland

Atomic layer deposition (ALD) is a coating technique capable of producing uniform material layers on complex surfaces. Although the ALD growth is extensively studied on inorganic substrates, less attention is being paid coating of polymeric materials. In addition to traditional polymeric 2D materials, it is interesting to study the growth and structure of films 3D substrates, such as electrospun fibres. Electrospinning is a process utilizing high voltage electric field to produce non-woven polymer fibres with diameters ranging from dozens of nanometres to several microns. In this study ex-situ NMR (nuclear magnetic resonance), is used to characterize the beginning ALD film growth on polymeric substrates.

In this study [1], we have used poly-L-lactic acid (PLLA) as a polymeric material in a form of a powder and electrospun fibres. Electrospinning was performed from commercial poly-L-lactic acid (Purasorb PL24), dissolved in CHCl₃ and DMF. The 1-500 cycles of Al₂O₃ films were made with Picosun R-200 ALD reactor from TMA (trimethylaluminium) and H₂O or O₃ at 80°C. Al₂O₃ coated PLLA powder was analysed by using solid state ²⁷Al NMR spectroscopy, in combination with NMR relaxometry, with aim to characterize the possible infiltration of the precursors inside the PLLA. Due to its quadrupolar nature ²⁷Al nucleus is extremely sensitive to changes in its local environment. It has also a high magnetic moment and a 100 % natural abundance, thus enabling the detection of very thin coatings. The effect of penetrated precursors inside PLLA particles to the proton longitudinal relaxation of PLLA was also studied. Additionally, coated materials were analysed with ATR-FTIR.

When electrospun PLLA fibres were coated with 500 cycles of TMA + O₃ and analysed with ATR-FTIR, we detected clear Al₂O₃ stretches. Spectra of parallel measurements were identical indicating the homogeneity of the deposited material. Furthermore, there was a new stretch (1614 cm⁻¹) in the spectrum with Al₂O₃ coating lacking from the spectrum of uncoated electrospun PLLA. The new stretch is probably from polymeric material reacting with the ALD precursors during the deposition. Further studies are needed with NMR, ATR-IR and in-situ QCM to elucidate the structure, growth and reactions between the ALD precursors and polymer more thoroughly.

[1] The research has received funding from the Academy of Finland, project ID 288212.

1:45pm **AF-MoA-2 Bulge Testing of Freestanding ALD Thin Film Membranes**, *Oili Ylivaara*, VTT Technical Research Centre of Finland, Finland; *P Törmä*, HS Foils, Finland; *I Stuns, J Saarihahti, R Puurunen*, VTT Technical Research Centre of Finland, Finland

Thin films made by atomic layer deposition (ALD) are ideal to be used as freestanding membranes in microelectromechanical system (MEMS) devices, as self-saturated surface reactions in ALD enable uniform and conformal film growth with precise thickness control. In applications, were ALD films are used as functional layers, thin film mechanical properties play in a crucial role as those enable design of reliable device structure. Here, the ultimate tensile strength (UTS), describing materials' ability to withstand external loads, is measured using bulge testing [1, 2] by pressurizing the membrane until the point where membrane breaks. The UTS is determined from the maximum breakage pressure. Studied ALD Al₂O₃ and TiO₂ films were grown on 380 µm thick double side polished RCA-cleaned (100) silicon wafers and targeted film thickness was about 100 nm. The films were grown in a top-flow ALD reactor, Picosun™ R-150, using temperature range from 110 to 300 °C. Freestanding ALD membranes were fabricated using isotropic xenon difluoride (XeF₂) etch process, which is purely chemical process, using silicon as sacrificial material. As UTS may depend on the membrane fabrication process, some of the freestanding membranes were fabricated also using deep reactive ion etching (DRIE). Through wafer etching, using DRIE, requires additional hard mask, as in XeF₂-process, photoresist withstands through wafer etching and no

Monday Afternoon, July 17, 2017

additional hard mask is required. This work continues the mechanical property characterization [2-6] started for ALD Al₂O₃ and TiO₂ on residual stress, elastic modulus, hardness and adhesion, and helps to deepen the knowledge about the influence of the process conditions (temperature) to mechanical properties of ALD thin films.

Acknowledgements: This work has been carried out within the Finnish Center of Excellence in Atomic Layer Deposition (ref. 251220) of the Academy of Finland.

[1] Berdova et al. *Acta Materialia* 66, 370 (2014)

[2] Berdova et al. *Journal of Vacuum Science and Technology A* 33, 01A106 (2015)

[3] Ylivaara et al. *Thin Solid Films* 552, 124 (2014)

[4] Lyytinen et al. *Wear* 342-343, 270 (2015)

[5] Kilpi et al. *Journal of Vacuum Science and Technology A* 34, 01A124 (2016)

[6] Ylivaara et al. *Journal of Vacuum Science and Technology A* 35, 01B105 (2017)

2:00pm **AF-MoA-3 Infiltrated Zinc Oxide in Polymethylmethacrylate: An Atomic Cycle Growth Study**, *Leonidas Ocola*, Argonne National Laboratory; *A Connolly*, Vassar College; *D Gosztola*, Argonne National Laboratory; *R Schaller*, Argonne National Laboratory, Northwestern University; *A Yanguas-Gil*, Argonne National Laboratory

We have investigated the growth of zinc oxide in a polymer matrix by sequential infiltration synthesis (SIS). The atomic cycle-by-cycle self-terminating reaction growth investigation was done using photoluminescence (PL), Raman and X-ray photoemission spectroscopy (XPS). Results show clear differences between Zn atom configurations at the initial stages of growth. Mono Zn atoms (O-Zn and O-Zn-O) exhibit pure UV emission with little evidence of deep level oxygen vacancy states (V_O). Dimer Zn atoms (O-Zn-O-Zn and O-Zn-O-Zn-O) show strong UV and visible PL emission from V_O states 20 times greater than that from the mono Zn atom configuration. After 3 precursor cycles the PL emission intensity drops significantly exhibiting first evidence of crystal formation as observed with Raman spectroscopy via the presence of longitudinal optical phonons. We also report a first confirmation of energy transfer between polymer and ZnO where the polymer absorbs light at 241 nm and emits at 360 nm, which coincides with the ZnO UV emission peak. Our work shows that ZnO dimers are unique ZnO configurations with high PL intensity, unique O_{1s} oxidation states, and sub-10 ps absorption and decay, which are interesting properties for novel quantum material applications.

- Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357, with the EXAFS data being collected at 9-BM-B. Work also supported by the University of Chicago Materials Research Center (MRSEC) IRG3-Engineering Quantum Materials and Interactions Contract #2-60700 – 95.

2:15pm **AF-MoA-4 Study on Atomic-Layer-Deposited Al₂O₃ Dielectric Films with a New Small Angle X-Ray Scattering Method**, *Chao Li, F Shahriarian, M Goorsky*, University of California Los Angeles

The porosity and pore size distribution of dielectric films deposited by atomic layer deposition (ALD) is important to understand their optical, mechanical and electrical properties. Advances in the development of X-ray generators and optics have made in-house small angle X-ray scattering (SAXS) experimentation suitable for the determination of sizes and shapes of pores (in the scale of sub-nanometer to several hundred nanometer) in thin films, which can be realized through the simulation of pore scattering based on distorted wave Born approximation. Previously, SAXS was widely applied to low-k dielectric films, with pore scattering determined with offset $\theta:2\theta$ scans using conventional 1-dimensional (1D) configuration of X-ray diffractometer. However, challenge still exists in estimating the diffuse scattering from surface roughness that also contributes to total diffuse scattering measured with offset $\theta:2\theta$ scans. In this study, we propose a new 1D SAXS method in which the scattering from surface roughness was determined by the simulation of X-ray reflectivity (XRR) longitudinal scan with parameters of RMS surface roughness σ , lateral correlation length ξ , and Hurst parameter h obtained from atomic force microscopy measurement, along with layer densities and compositional grading

determined by specular XRR simulation. This new SAXS method was validated with scanning electron microscope using a single-layer porous InP sample, and was utilized to reveal the effects of ALD parameters on pore size distribution of single-layer Al₂O₃ dielectric films. Two Al₂O₃ single layers were deposited on Si substrates with different parameters of ALD that is a good candidate for dielectrics films in various applications, due to the self-limiting nature of chemical reactions resulting in the precise control of film thickness and large-area uniformity. Both of them have amorphous structures. It is indicated by the new SAXS method that the #1 Al₂O₃ film is porous with a mean pore size of 19 ± 1.8 nm along the out-of-plane direction, while there are no pores in the #2 Al₂O₃ film. This correlates with the specular XRR showing a lower density (2.95 ± 0.01 g/cm³) of the #1 Al₂O₃ film than that (3.01 ± 0.01 g/cm³) of the #2 Al₂O₃ film. In addition, 2-dimensional (2D) glancing incidence SAXS (GISAXS) measurements also suggest the absence of pore scattering for the #2 Al₂O₃ film while the #1 Al₂O₃ film to be porous, agreeing with the new 1D SAXS method. Besides, a mean pore size of approximately 2 ± 0.2 nm along the in-plane direction of the #1 Al₂O₃ film was also suggested by 2D GISAXS.

2:30pm AF-MoA-5 Evaluating Mechanical Properties of Free-standing ALD Al₂O₃, Junmo Koo, Korea University, Republic of Korea; *S Lee, T Kim*, Korea Advanced Institute of Science and Technology, Republic of Korea; *J Shim*, Korea University, Republic of Korea

Recently, atomic layer deposition (ALD) has been widely used in various fields due to its unique characteristics. Film thickness and composition can be precisely manipulated by controlling the number of ALD cycles in the atomic scale. In addition, ALD can produce large area thin films without pinholes or defects even in complex structures such as nano-trenches and three-dimensional porous media.^[1] ALD Al₂O₃ is one of the most actively used materials in various fields such as gate dielectrics, memory and capacitors, encapsulation of organic displays and solar cells, and chemical protection.^[2] For this reason, understanding the mechanical properties of ALD Al₂O₃ is expected to be of great help in developing robust and reliable devices.

A number of studies have been conducted to determine the mechanical properties of ALD Al₂O₃ using a variety of methods including nano-indentation and bulge testing.^[3] However, many of these methods are performed with the ALD film bonded to the substrate, where it is difficult to completely eliminate the influence of the substrate properties. In particular, the stiffness and roughness of the substrate are known to have a significant effect on the Young's modulus and hardness measurements of the films.^[4] In this study, we have evaluated free-standing ALD films completely separated from the wafer.^[5] We have successfully measured the Young's modulus, tensile strength and elongation of ALD Al₂O₃ thin films (~130 nm in thickness) deposited at temperatures of 80-250 °C. In this presentation, we will discuss in detail the recent progress and results of our research.

References

- [1] J.H. Shim, S. Kang, S.W. Cha, W. Lee, Y.B. Kim, J.S. Park, T.M. Gür, F.B. Prinz, C.C. Chao, *J. Mater. Chem. A* 1, 12695 (2013)
- [2] S.M. George. *Chem. Rev.* 110, 111 (2010)
- [3] M.K. Tripp, C. Stampfer, D.C. Miller, T. Helbling, C.F. Herrmann, C. Hierold, K. Gall, S.M. George, V.M. Bright. *Sens. Actuators. A* 130, 419 (2006)
- [4] D.C. Miller, R.R. Foster, S.-H. Jen, J.A. Bertrand, S.J. Cunningham, A.S. Morris, Y.-C. Lee, S.M. George, M.L. Dunn. *Sens. Actuators. A* 164, 58 (2010)
- [5] J.-H. Kim, A. Nizami, Y. Hwangbo, B. Jang, H. Lee, C. Woo, S. Hyun, T.-S. Kim. *Nat. Commun.* 4:2520 (2013)

2:45pm AF-MoA-6 Secondary Electron Yield of Nano-oxide Thin Films Measured by Spherical Collector with Pulsed Electron Irradiation, Baojun Yan, *S Liu, K Wen*, Institute of High Energy Physics of Chinese Academy of Sciences, China

As a solid-state detector, electron multipliers coated with high secondary electron yield (δ) materials have the potential to provide a significant improvement over existing devices. Nano-oxide thin films, such as aluminum oxide (Al₂O₃) and magnesium oxide (MgO), with high δ were deposited via atomic layer deposition technique. The δ of nano-oxide thin films were measured by spherical collector with pulsed electron irradiation in high vacuum condition. The influences of incident electron energy (100 eV ~ 1 KeV), incident electron angle (0° ~ 85°), sample thickness (3 nm ~ 100 nm) and annealing temperature (25°C ~ 200°C) on δ have been investigated in this study and the time evolution of δ also has been

investigated under the pulsed electron irradiation. The mechanism of improving the δ of the insulating material has been discussed.

3:00pm AF-MoA-7 Electrical Characterization of Platinum Thin Films Deposited by Plasma-Enhanced ALD and Magnetron Sputtering, Martin Winterkorn, *H Kim, K Kaplan, J Provine, T Kenny, F Prinz*, Stanford University

Platinum is widely used in sensing applications such as thermistors, bolometers or thermal accelerometers due to its desirable thermal, electrical and chemical properties, including a high temperature coefficient of resistance (TCR), low 1/f noise, high melting point and chemical inertness. With the ability to synthesize ultra-thin pinhole-free layers with high conformality, Atomic Layer Deposition of platinum enables an even wider range of usages and fabrication processes. However, ALD of platinum also has several disadvantages compared to traditional deposition techniques, most notably low growth rate, high precursor cost and incorporation of carbon impurities into the film from unreacted precursor ligands. In this work, we compare the properties of platinum thin films from plasma-enhanced ALD (PEALD) and magnetron sputtering in an intermediate thickness regime of around 30 nm, deposited on flat thermally oxidized Si substrates.

Particular characterization and optimization effort has been put on electrical properties as those are of prime importance for sensing applications. A resistivity close to the bulk value (10.6 μΩcm) indicates a low density of impurities and other scattering sites, which correlates with better stability and higher TCR.

Sputtered films were prepared in a multipurpose sputtering system by Kurt J. Lesker Company, which is capable of both DC and RF magnetron sputtering with variable plasma power, Argon gas pressure, substrate temperature and substrate bias. Due to the large number of process parameters, a non-factorial design-of-experiments approach was used to optimize the deposition conditions for low resistivity. A summary of the first-order dependencies found is shown in Table 1. A maximum substrate temperature of 270°C was used to be comparable to the non-annealed ALD films.

PEALD of platinum was accomplished by sequential introduction of remote O₂ plasma and trimethyl(methylcyclopentadienyl)platinum(IV) precursor, performed in an Ultratech / Cambridge Nanotech Fiji ALD reactor. A variation of this base recipe with additional cycle-by-cycle H₂ and O₂ plasma treatment has shown to significantly improve film adhesion as tested by tape lift-off. Both films were deposited at 270°C and post-deposition, rapid thermal annealed at various temperatures for 5 minutes in a N₂ ambient. Figure 1 shows the film resistivities as a function of anneal temperature, with 270°C indicating no anneal. The overall findings are summarized in Figure 2. Further characterization of film morphology using AFM and TEM as well as resistivity stability is currently underway.

3:15pm AF-MoA-8 A Facile Control of Major Carriers on Atomic Layer Deposited SnO_x Thin Film by using Various Oxygen Reactants, Jung-Hoon Lee, Hanyang University, Republic of Korea; *J Park, J Park*, Hansol Chemical, Republic of Korea; *J Park*, Hanyang University, Republic of Korea

Oxide semiconductor materials have attracted attention for application in thin film transistors (TFT), solar cells, gas sensors, and lithium batteries. A great number of experimental studies have been conducted for a n-type semiconductor such as ZnO, In₂O₃, InGaZnO, ZnSnO, but p-type materials such as Cu₂O, NiO, SnO are rarely studied due to their stability. However, since needs of p-type materials are increased in electronic device for p-n junctions, complementary metal-oxide semiconductors (CMOS). SnO is one of good candidate for p-type material because it has high mobility and wide band gap, which can be used to fabricate transparent device.

In our study, SnO_x thin film was deposited by thermal atomic layer deposition (ALD) method using N,N'-tert-butyl-1,1-dimethylethylenediamine stannylene as a precursor, Ozone and Water as a reactant. Both processes using ozone, water show surface limit reaction behavior as increase precursor temperature with constant purge time 10s during processes. Growth rate is different a lot; it can be caused from different surface functional group state derived from different reactant. Absorbance and refractive index of SnO_x thin films are investigated using ultraviolet-visible spectroscopy (UV-VIS) and spectroscopic ellipsometry (SE), respectively. SnO_x using ozone and water have 3.60-3.17, 2.24-2.30 eV of optical band gap and ~2.0, ~2.6 refractive index, which are correspond to SnO₂, SnO, respectively. SnO exhibit p-type characteristic confirmed by Hall measurement and has carrier concentration about 10¹⁸. Furthermore, we can optimize SnO, SnO₂ processes and use them for TFT, p-n diode, CMOS application

Monday Afternoon, July 17, 2017

4:00pm **AF-MoA-11 Activation of Metal Amidinate ALD Precursors on Surfaces and Implications for Film Growth**, *B Chen*, University of California, Riverside; *Y Duan*, University of Delaware; *Y Yao*, University of California, Riverside; *J Coyle*, *S Barry*, Carleton University, Canada; *A Teplyakov*, University of Delaware; **Francisco Zaera**, University of California, Riverside

Finding good metallorganic compounds with clean chemistry for the growth of metal films has proven challenging. Amidine ligands have shown some promise for this application because they are stable and form volatile complexes with most metals. Unfortunately, although the clean displacement of amidine ligands from metal complexes on solid surfaces should be facile, most studies carried out to date on the use of metal amidinates for metal film growth have pointed to the incorporation of significant amounts of impurities, a sign of extensive decomposition of the ligand upon activated adsorption.

Here, we discuss a potential reason for this behavior, namely, the fact that the metal amidinate complexes form dimers or tetramers, and that those adsorb on surfaces via side bonds with nitrogen atoms and cannot be fully decoupled unless using the higher temperatures that also favor ligand decomposition.

Specifically, the gas-phase structure of three copper amidinate compounds, copper(I)-N,N'-di-sec-butyl-acetamidinate (**1**), copper(I)-N-sec-butyl-2-iminopyrrolidinate (**2**), and copper(I)-N-tert-butyl-5,5-dimethyl-2-iminopyrrolidinate (**3**), and their initial adsorption on silicon oxide surfaces were characterized by a combination of experimental measurements and density-functional theory (DFT) calculations. Liquid-injection field desorption ionization mass spectrometry (LIFDI-MS) data proved that the dimer and tetramer structures that these compounds adopt in solid phase are retained upon vaporization into the gas phase (dimers for the first and third compounds, a tetramer for the second). Results from DFT calculations of the relative energies of formation of the monomers, dimers, and tetramers, confirmed the experimental results. Adsorption on the surface of silicon oxide films was determined, based on additional DFT calculations, to lead to the binding of the copper amidinates preferentially as dimers; although the monomers form stronger bonds to the silicon surface because they bind directly through their copper atom, this cannot fully compensate for the large energy required to break the dimers apart. N 1s x-ray photoelectron spectroscopy (XPS) data were used to corroborate both the presence of the dimers on the surface with the second (**2**) precursor and the threshold for their surface decomposition around room temperature. The behavior of the third compound is somewhat more complex, with some decomposition possibly happening immediately upon adsorption at 100 K.

Results from additional studies will be presented to analyze the role of the nature of the solid substrate in defining the precursor activation chemistry.

4:15pm **AF-MoA-12 Surface Chemistry during Atomic-Layer Deposition of Pt Studied with Vibrational Sum-frequency Generation**, **Vincent Vandalon**, *A Mackus*, *W Kessels*, Eindhoven University of Technology, Netherlands

The reaction mechanism of Pt atomic-layer deposition (ALD) using MeCpPtMe₃ as precursor and O₂ as co-reactant was investigated with vibrational broadband sum-frequency generation (BB-SFG) spectroscopy. Pt nanoparticles and ultrathin films synthesized by ALD have a wide range of potential applications because of the chemical stability, catalytic nature, and high work function of Pt. Moreover, the Pt ALD process can be considered as a model system for noble metal ALD. Insight into the growth mechanism of these noble metal ALD processes is essential for extending the operating conditions or for enabling new applications. However, to gain fundamental understanding of the growth mechanism, an analysis technique is needed which can directly study the surface chemistry during ALD.

Vibrational BB-SFG spectroscopy is excellently suited for in-situ studies of the surface chemistry governing ALD because of its inherent interface selectivity, submonolayer sensitivity, and short acquisition times. It is a nonlinear optical technique which uses the mixing of picosecond visible and femtosecond mid-IR pulses to probe the vibrational response of surface groups. The unique nature of BB-SFG spectroscopy allows the in-situ investigation of the surface chemistry on both reflective (i.e. Pt metal) and transparent substrates without any modifications to the setup.

Although the Pt ALD process serves as a model system, several questions about the underlying reaction mechanism remain. For example, it is not clear which species of hydrocarbons are present on the surface. In this work, direct evidence for the presence of CH₃ groups during ALD will be presented. Moreover, a contribution assigned to species containing C=C

bonds was observed, originating from the MeCp ligand. This assignment was confirmed in a series of experiments exposing different surfaces (Pt and SiO₂) to either the MeCpPtMe₃ precursor or to CH₃-C₅H₇, a molecule similar to the MeCp ligand. For ALD at 250 C, both the CH₃ and the C=C groups were observed on the surface after the precursor half-cycle and both were removed in the subsequent O₂ half-cycle. The relative CH₃ and C=C coverage after the precursor half-cycle was studied from 80 C up to 300 C. The CH₃ coverage showed a monotonic decrease with temperature whereas the C=C coverage was fairly constant. Furthermore, the reaction kinetics during the precursor half-cycle were studied, revealing that the saturation of C=C groups occurred ~ 3 times faster than that of the CH₃ groups. Both the temperature trend and the reaction kinetics are evidence for the dehydrogenation of some of the hydrocarbon species on the Pt surface during ALD.

4:30pm **AF-MoA-13 Mechanistic Study of the Atomic Layer Deposition of Titanium Dioxide Films from Ethylcyclopentadienyltris(dimethylamido)titanium and Ozone or Water**, **Joseph Klesko**, *R Rahman*, *A Dangerfield*, *C Nanayakkara*, *T L'Esperance*, University of Texas at Dallas; *C Dezelah*, *R Kanjolia*, EMD Performance Materials; *Y Chabal*, University of Texas at Dallas

A plethora of Ti precursors are widely available. However, many generate corrosive reaction byproducts (e.g. Ti halides), suffer from low thermal stability (e.g. alkylamides like Ti(NMe₂)₄), or exist as solids and consequently increase the risk of particle incorporation into the growing film (e.g. alkoxides like Ti(OMe)₄). Heteroleptic cyclopentadienyl-based Ti precursors have increased thermal stability over their homoleptic alkylamide or alkoxide analogues.¹ Herein, a mechanistic study is presented of the ALD of titanium dioxide films grown from ethylcyclopentadienyltris(dimethylamido)titanium (TIECTA) and either ozone or water.

TIECTA was selected because it is a liquid, halogen-free precursor that is thermally-stable under inert conditions. A comparison analysis of the ALD processes between ozone and water as co-reactants was performed. In both cases, TIECTA initially reacts with the OH-terminated Si(111)-SiO₂ substrates at 150 °C and remains thermally stable up to 350 °C. Using spectroscopic ellipsometry and X-ray photoelectron spectroscopy (XPS), an ALD window was found to be approximately 250–300 °C with a deposition rate of ~1 Å/cycle with ozone, while with water there is an apparent deposition rate of approximately 0.6 Å/cycle with no obvious ALD window. *In-situ* Fourier transform infrared spectroscopy (FTIR) revealed a clear ligand exchange for the ozone process, with the formation of intermediate Ti-formate (1614 cm⁻¹) and -carbonate (1580 cm⁻¹) species upon ozone exposure,² and CH₃ absorption after TIECTA exposure. In contrast, ligands associated with the water process were difficult to measure, preventing the formulation of an exact mechanism. XPS further showed that films grown within the ALD window using ozone contained no detectable carbon after 5 s of argon ion sputtering, while films grown with water at 300 °C contained ≤3 at.% carbon.

References

1. Rose, M.; Niinisto, J.; Michalowski, P.; Gerlich, L.; Wilde, L.; Endler, I.; Bartha, J. W. *J. Phys. Chem. C* **2009**, *113*, 21825–21830.
2. Bernal Ramos, K.; Clavel, G.; Marichy, C.; Cabrera, W.; Pinna, N.; Chabal, Y. J. *Chem. Mater.* **2013**, *25*, 1706–1712.

4:45pm **AF-MoA-14 The Role of Surface Chemical Functionality in the Initial Stages of Deposition for Copper and Silver Precursors**, **Andrew Teplyakov**, University of Delaware

Copper and silver deposition onto solid substrate forms a foundation for multiple applications, from catalysis to microelectronics and photonics. The key practical issue in the deposition process is the formation of the interface between the metal deposited and the substrate material. The control over the formation of this interface in chemical deposition schemes depends on the possibility to tune the chemical reactions leading to the deposition. This in turn depends on the actual surface functionalities available and their distribution on the surface. Thus, understanding and controlling these reactions is of paramount importance for producing the desired interfaces.

Chemical interactions of several copper and silver deposition precursor molecules with functionalized silicon, silica, ZnO, and carbon (ordered pyrolytic graphite, HOPG) surface will be discussed targeting specifically the chemistry of adsorption and decomposition depending on the precursor ligands and oxidation states of the metal. The study considers surface chemical functional groups available on the surfaces of these different

Monday Afternoon, July 17, 2017

materials and the mechanistic understanding is supported by microscopic (atomic force microscopy, scanning electron microscopy, transmission electron microscopy) and spectroscopic (X-ray photoelectron spectroscopy, time of flight secondary ion mass spectrometry, and infrared spectroscopy) methods supported by the density functional calculations. The work with copper deposition precursors targets $\text{Cu}(\text{acac})_2$, $\text{Cu}(\text{hfac})_2$, and $\text{Cu}(\text{hfac})\text{VTMS}$. The more challenging and far less investigated reactions of silver precursor molecules are mostly focused on trimethylphosphine(hexafluoroacetylacetonato)silver(I). These molecules possess very different reactivities with respect to different surface functionalities and substrates; however, understanding the mechanisms of surface reactions allows one to direct the deposition to prepare surface metallic nanostructures and thin films with well-defined interfaces between the metals deposited and underlying substrates.

5:00pm AF-MoA-15 Reaction Mechanism of ALD Zirconium Oxide using Alkylamido-Cyclopetadienyl Zirconium Precursors, Jae-Min Park, T Mayangsari, S Kim, Y Kim, Sejong University, Republic of Korea; W Han, B Yoo, W Koh, UP Chemical Co., Ltd., Republic of Korea; W Lee, Sejong University, Republic of Korea

Zirconium oxide thin films are used as the high dielectric constant material in dynamic random access memory (DRAM) devices. ALD technique has been used because of good step coverage, precise control of film thickness, and high film quality, and alkylamido-cyclopetadienyl zirconium compounds, such as $\text{CpZr}(\text{NMe}_2)_3$, are used as the zirconium precursor. As the aspect ratio of the DRAM capacitor continue to increase to >50 in the state-of-art DRAMs, however, the zirconium precursor with higher reactivity and thermal stability is requested for improving step coverage [1]. In the present work, we investigate reaction mechanism of ALD zirconium oxide using different alkylamido-cyclopetadienyl zirconium compounds and ozone. Density functional theory calculation is used for expecting the characteristics of the precursors with different structures and ligands. The deposition kinetics and the reaction mechanism were investigated for different precursors by in-situ QCM and FTIR. The physical and electrical properties of the deposited films were also characterized.

[1] J. Niinistö, et al, *J. Mater. Chem.*, 18 (2008) 5243.

5:15pm AF-MoA-16 Elucidation of Distinct Electric Characteristics of ALD Oxides on Highly Ordered GaAs(001) and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$ Surfaces using Synchrotron Radiation Photoelectron Spectroscopy, Yi-Ting Cheng, National Chia-Yi University, Republic of China; W Chen, National Synchrotron Radiation Research Center, Republic of China; K Lin, L Young, Y Lin, H Wan, National Taiwan University, Republic of China; T Pi, National Synchrotron Radiation Research Center, Republic of China; M Hong, National Taiwan University, Republic of China; C Cheng, National Chia-Yi University, Republic of China; J Kwo, National Tsing Hua University, Republic of China

The frequency dispersion at accumulation in the capacitance-voltage (CV) curves has long been noted to behave differently between n- and p-type (In)GaAs MOS capacitors. In Fig. 1 (a)-(c), the dispersion is greater in n-GaAs(001) than that in p-GaAs, while greater in p- $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$ than that in n-InGaAs. This is irrespective of the atomic-layer deposited (ALD) oxides.^{1,2} We have solved the puzzles by investigating the surface electronic structure of as-grown MBE GaAs(001)-4x6 and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$ -4x2, and later using the noble metals as the probed adatoms to simplify the atom-to-atom interaction. The characterization method is synchrotron radiation photoelectron spectroscopy, which is a powerful tool to probe the charge environments of the surface atoms prior to and after the ALD oxide depositions, namely the interfacial electronic characteristics. We always kept the samples under UHV throughout the experiments. The Pauling electronegativity of As, Ga, Ag, and Au is 2.18, 1.81, 1.93, and 2.54, respectively. Intuitively, the contact of As and Au atoms would result in a charge transfer from As to Au. The induced peak of As 3d core level should appear in a higher binding energy (BE), the ordinal energy position of the contacted As atoms. However, we found that the induced As 3d component actually lies at lower BE as shown in Fig. 2. In other words, the III-V surfaces show high Pauling electronegativity. This unique property alone is still unable to resolve the issue of different dispersion behavior in between GaAs(001)-4x6 and InGaAs(001)-4x2. We further notice that the surface electronic structure is not entirely the same in them. The As atoms in the top As-In-As rows on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$ -4x2 are enriched in charge due to surface reconstruction,³ while those in the faulted terrace of the GaAs(001)-4x6 are deficient in charge.¹

Now, it becomes clear that if the surface As atoms are not properly passivated, they will serve as charge trappers to the ones accumulated at

the oxide/(In)GaAs interface, namely, electrons in n-GaAs and holes in p-InGaAs MOS. Indeed, upon deposition of 10-cycles TMA and H_2O precursors onto a GaAs(001)-4x6 surface, a great percentage of the unbonded surface As atoms were still observed in Figs. 3-4. In Figs. 5-6, the case is similar for 10-cycles tetrakis(ethylmethylamino) hafnium (TEMAHF) and H_2O onto a InGaAs(001)-4x2 surface. We will illustrate how the ALD precursors react with (In)GaAs surface atoms in an atomic scale.

¹T.W. Pi, et. al., *Nanotechnology***26**, 164001 (2015).

²T.D. Lin, et. al., *Appl. Phys. Lett.***100**, 172110 (2012).

³T.W. Pi, et. al., *Appl. Phys. Lett.***104**, 042904 (2014).

Author Index

Bold page numbers indicate presenter

— B —

Barry, S: AF-MoA-11, 3

— C —

Chabal, Y: AF-MoA-13, 3

Chen, B: AF-MoA-11, 3

Chen, W: AF-MoA-16, 4

Cheng, C: AF-MoA-16, 4

Cheng, Y: AF-MoA-16, **4**

Connolly, A: AF-MoA-3, 1

Coyle, J: AF-MoA-11, 3

— D —

Dangerfield, A: AF-MoA-13, 3

Dezelah, C: AF-MoA-13, 3

Duan, Y: AF-MoA-11, 3

— G —

Goorsky, M: AF-MoA-4, 1

Gosztola, D: AF-MoA-3, 1

— H —

Han, W: AF-MoA-15, 4

Heikkilä, P: AF-MoA-1, 1

Hong, M: AF-MoA-16, 4

— K —

Kanjolia, R: AF-MoA-13, 3

Kaplan, K: AF-MoA-7, 2

Kenny, T: AF-MoA-7, 2

Kenttä, E: AF-MoA-1, 1

Kessels, W: AF-MoA-12, 3

Kim, H: AF-MoA-7, 2

Kim, S: AF-MoA-15, 4

Kim, T: AF-MoA-5, 2

Kim, Y: AF-MoA-15, 4

Klesko, J: AF-MoA-13, **3**

Koh, W: AF-MoA-15, 4

Koo, J: AF-MoA-5, **2**

Kwo, J: AF-MoA-16, 4

— L —

L'Esperance, T: AF-MoA-13, 3

Lee, J: AF-MoA-8, **2**

Lee, S: AF-MoA-5, 2

Lee, W: AF-MoA-15, 4

Li, C: AF-MoA-4, **1**

Lin, K: AF-MoA-16, 4

Lin, Y: AF-MoA-16, 4

Liu, S: AF-MoA-6, 2

— M —

Mackus, A: AF-MoA-12, 3

Mayangsari, T: AF-MoA-15, 4

— N —

Nanayakkara, C: AF-MoA-13, 3

— O —

Ocola, L: AF-MoA-3, **1**

— P —

Park, J: AF-MoA-15, **4**; AF-MoA-8, 2

Pi, T: AF-MoA-16, 4

Prinz, F: AF-MoA-7, 2

Provine, J: AF-MoA-7, 2

Putkonen, M: AF-MoA-1, 1

Puurunen, R: AF-MoA-2, 1

— R —

Rahman, R: AF-MoA-13, 3

Rautkoski, H: AF-MoA-1, 1

— S —

Saarihahti, J: AF-MoA-2, 1

Schaller, R: AF-MoA-3, 1

Shahriarian, F: AF-MoA-4, **1**

Shim, J: AF-MoA-5, 2

Simell, P: AF-MoA-1, 1

Stuns, I: AF-MoA-2, 1

Svärd, L: AF-MoA-1, 1

— T —

Teplyakov, A: AF-MoA-11, 3; AF-MoA-14, **3**

Törmä, P: AF-MoA-2, 1

— V —

Vandalon, V: AF-MoA-12, **3**

Virtanen, T: AF-MoA-1, 1

— W —

Wan, H: AF-MoA-16, 4

Wen, K: AF-MoA-6, 2

Winterkorn, M: AF-MoA-7, **2**

— Y —

Yan, B: AF-MoA-6, **2**

Yanguas-Gil, A: AF-MoA-3, 1

Yao, Y: AF-MoA-11, 3

Ylivaara, O: AF-MoA-2, **1**

Yoo, B: AF-MoA-15, 4

Young, L: AF-MoA-16, 4

— Z —

Zaera, F: AF-MoA-11, **3**