

Monday Afternoon, October 28, 2013

Thin Film

Room: 104 A - Session TF+AS+SE+SS-MoA

ALD/MLD Surface Reactions, Precursors, and Properties

Moderator: R.K. Grubbs, Sandia National Laboratories, J.S. Jur, North Carolina State University

2:00pm **TF+AS+SE+SS-MoA1 Growth of Metallic First Row Transition Metal Films by Atomic Layer Deposition from New Precursors, C.H. Winter, L.C. Kalutara, Wayne State University**
INVITED

Our laboratory seeks to develop the growth of metallic first row transition metal thin films using atomic layer deposition (ALD). The microelectronics industry is calling for the growth of metallic first row transition metal films by the ALD method for a variety of applications, including copper metallization, seed layers for copper metallization, copper/manganese alloys for self-forming copper diffusion barriers, and magnetic alloys. The ALD growth of noble metal thin films has been explored extensively in the past ten years, due to the positive electrochemical potentials of these metal ions and relative ease of reduction to the metallic state.¹ The low temperature ALD of high purity, low resistivity Cu films has been described,² but ALD routes to the other metallic first row transition metal films remain poorly developed, largely because of the negative electrochemical potentials of most of the ions and a corresponding lack of powerful reducing co-reagents that can convert precursors in positive oxidation states to the metals. We will describe the synthesis, structure, and properties of a large series of new first row transition metal ALD precursors containing alkoxide ligands that combine high volatilities, high thermal stabilities, and high reactivities toward reducing agents. We will also report borane reducing agents that can react with the metal precursors to afford metallic films. Additionally, we will overview the thermal growth of metallic copper, nickel, cobalt, iron, manganese, and chromium thin films from these new precursors. Key advances include development of optimized ALD precursors with very similar ligands and chemistry, and identification of new reducing co-reagents that can rapidly reduce the positive oxidation state precursors to the metals.

1. M. Leskelä, M. Ritala, O. Nilsen, *MRS Bull.* **2011**, 36, 877-884.
2. B.H. Lee, J.K. Hwang, J.W. Nam, S.U. Lee, J.T. Kim, S.-M. Koo, A. Baunemann, R.A. Fischer, M.M. Sung, *Angew. Chem. Int. Ed.* **2009**, 48, 4536-4539. T.J. Knisley, T.C. Ariyasena, T. Sajavaara, M.J. Saly, C. H. Winter, *Chem. Mater.* **2011**, 23, 4417-4419.

2:40pm **TF+AS+SE+SS-MoA3 O₂ based Ru ALD using CpRu(CO)₂Et: First-principles, Experiments and Micro-kinetic Modeling. C.K. Ande, N. Leick, Eindhoven University of Technology, Netherlands, S.D. Elliott, Tyndall National Institute, Ireland, W.M.M. Kessels, Eindhoven University of Technology, Netherlands**

In the present work, we use a combination of first-principles calculations, QMS experiments and micro-kinetic modeling to reveal the reactive pathways in operation during an O₂ based Ru ALD using CpRu(CO)₂Et as the metal precursor. Analysis of the gas phase species in our QMS experiments showed that the surface chemisorption of CpRu(CO)₂Et resulted in the formation of dehydrogenation and combustion products such as H₂, CO₂, CO and H₂O. H₂ was detected as a major surface reaction product during the metal precursor pulse. Strikingly, during the O₂ pulse virtually no H₂, H₂O or other H-containing reaction products were measured. These results suggest that a number of surfaces might be involved: bare, O-covered Ru and RuO₂ surfaces (Leick et al. *Chem. Mat.*, 24, 3696, (2012)).

While it is still experimentally difficult to accurately identify the surface and reactions happening at the surface, Density Functional Theory (DFT) provides an elegant way to study the same. Therefore, we used DFT calculations to study the role of bare and O-covered surfaces on dehydrogenation reactions during the ALD process. Since most of the dehydrogenation occurs from the Et and Cp ligands, as a first step, we studied dehydrogenation of ethane. In order to probe the role of O-covered surfaces in the dehydrogenation reactions, we studied the reactions on both bare (Ru(0001)) and O-covered (0.25 ML and 0.5 ML) Ru surfaces. It is clear from the calculations that the dehydrogenation on the bare Ru(0001) is the most energetically favorable process. Interestingly, they also show that the presence of O on the Ru(0001) surface inhibits the dehydrogenation reactions from taking place. Thus, dehydrogenation reactions happening on O-rich patches of the growing Ru surface can be excluded.

Although DFT calculations provide accurate energy changes and activation energies of each of the possible elementary reactions, they still do not predict the collective behavior when all the processes are possibly happening simultaneously. To resolve this problem we use micro-kinetic modeling and go up to the next higher length and time scales in an ALD process. In micro-kinetic modeling, information about elementary reactions that happen at the gas surface interface is used to describe the overall time evolution of the system which includes species in the gas phase and on the surface. We use accurate activation energies obtained from our DFT calculations in the micro-kinetic model. Preliminary results clearly show the evolution of H₂ from the decomposition of ethane. We hope to extend the method and present results about the decomposition of the complete precursor on the bare Ru(0001) surface.

3:00pm **TF+AS+SE+SS-MoA4 The Chemistry of the Cu(I) s-Butyl Amidinate Atomic Layer Deposition (ALD) Precursor on Ni and Cu Surfaces, Y. Yao, T. Kim, J. Coyle, S.T. Barry, F. Zaera, University of California, Riverside**

Thanks to the self-limiting and complementary nature of the reactions involved, atomic layer deposition (ALD) has become a promising method for making uniform and conformal thin films. Cu(I) amidinates have been introduced in recent years as promising precursors for the ALD of copper interconnects. An understanding of the surface chemistry of these copper(I) amidinates is essential to the design of the corresponding ALD processes. Here we report the results from our studies on the surface chemistry of Cu(I) s-butyl amidinate on Ni and Cu surfaces using X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD).

It was determined that, on Ni surfaces, the reduction of Cu(I) to metallic Cu happens already at room temperature. The Cu(I) s-butyl amidinate adsorbs dissociatively on those Ni surfaces, and decompose thermally to produce H₂, HCN and N₂, at about 500 K, 570 K and 830 K, respectively. After annealing to temperatures above 800 K, all N-containing species desorb as HCN or N₂, but some carbon left on the surface. It was found that Cu(I) s-butyl amidinate adsorption on Ni between 300 K and 400 K is self-limited, with an estimated Cu saturation coverage of 0.15 ML, but switches above 500 K to a behavior where continuous copper deposition occurs, as typically seen in chemical vapor deposition (CVD) processes. It was also found that surface oxygen on Ni substrates exerts a great effect on the surface chemistry of the Cu precursor. On oxygen covered Ni surface, the Cu(I) reduction to metallic Cu only happens above 500 K, at which point the Ni surface oxide is reduced by the organic surface species that result from Cu(I) s-butyl amidinate adsorption to form H₂O and CO₂. The presence of surface oxygen greatly reduces the carbon deposition in the annealing process.

On Cu surfaces, which form after several ALD cycles on any substrate, the Cu(I) s-butyl amidinate precursor shows less activity than on Ni surfaces. The molecule adsorbs molecularly on Cu at 300 K, and the Cu(I) center is reduced to metallic Cu only after annealing above 500 K. Chemisorbed Cu(I) s-butyl amidinate starts to dissociate at about 460 K, via the breaking of a C-N bond and the formation of pyrrolaminium (C₄H₇N₂) and butene. H₂ desorption is detected at about 510 K, and HCN and N₂ desorption above 800 K. As on Ni surfaces, self-limited copper uptake on Cu substrates takes place between 300 K and 400 K, with an estimated Cu saturation coverage of 0.06 ML, and changes to CVD above 500 K. On O/Cu(110), H₂O desorption peaks at 470 K and a broad CO₂ desorption feature is seen between 450 K and 600 K. H₂ desorption was detected at 595 K.

3:40pm **TF+AS+SE+SS-MoA6 Quantitative In Situ Infrared Analysis of Reactions between Trimethylaluminum and Polymers during Al₂O₃ Atomic Layer Deposition, G.N. Parsons, B. Gong, P.S. Williams, North Carolina State University**

The reactions of trimethylaluminum (TMA) toward substrates during the Al₂O₃ atomic layer deposition (ALD) on a variety of polymers were studied by in-situ Fourier transform infrared spectroscopy (FTIR). The experiments demonstrate that TMA reacts with certain nucleophilic functional groups on the polymer surface during the first several ALD cycles. For some polymer substrates, TMA vapor penetrates into the polymer and reacts in the polymer bulk. In both cases, the initial reaction plays an important role in the nucleation and growth of Al₂O₃. For chemically inert polymers nucleation of Al₂O₃ ALD is relative slow at the initial stage due to the lack of reactive groups on the substrate. However, polyester, polyamide and polyether are more reactive, and in-situ FTIR spectra showed a larger extent of reaction with TMA, facilitating the nucleation of ALD film on these polymers. By comparing FTIR spectra, we quantitatively estimate the extent of TMA reaction towards different polymers, and confirmed the results using X-ray photoelectron spectroscopy and scanning electron microscopy. Results give insight into the importance of polymer structure in determining

the nature and extent of reaction during ALD film processing on polymer substrates.

4:00pm TF+AS+SE+SS-MoA7 Surface Reactions during the ALD of TiO_2 on Si and GaAs Surfaces Studied by *In Situ* ATR-FTIR, L. Ye, T. Gougousi, University of Maryland, Baltimore County

The atomic level mechanisms during the deposition of TiO_2 on etched and chemical oxide Si (100) and GaAs (100) surfaces from tetrakis dimethyl amino titanium (TDMAT) and H_2O at 100 and 200C have been studied using *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The adsorption of TDMAT on Si and GaAs surfaces is confirmed by the observation of CH and NC vibration modes. Exposure to H_2O removes most of the CH bonds, but species associated with reaction by-products remain on the surface and increase in intensity as the deposition progresses. For the deposition on both chemical oxide and hydrogen terminated Si surfaces at 100 and 200C, the amount of TDMAT adsorbed on the surfaces generally decreases with increasing number of cycles and reaches similar steady state coverage at about the 20th cycle of deposition. For depositions on hydrogen terminated Si surfaces, about 50% of the initial Si-H bonds remain unreacted after 20 process cycles. For deposition on both Si and GaAs surfaces, C=O bonds at 1595 cm^{-1} associated with formate species accumulate during the deposition. The use of GaAs internal reflection elements allows extension of the useful range just around 700 cm^{-1} permitting possible observation of the precursor reaction with the surface As and Ga oxides.

4:20pm TF+AS+SE+SS-MoA8 Metal Oxide/Carbon Composite Films by Pyrolysis of Hybrid Organic-Inorganic MLD Films, J. Travis, S.M. George, University of Colorado at Boulder

Many metal oxides with desirable electrochemical properties have limited use in electrochemical devices due to their low electrical conductivities. One way to improve the electrical conductivity is to integrate carbon domains as a conductive additive in the metal oxide. We have developed a method to produce metal oxide/carbon composite thin films via pyrolysis of hybrid organic-inorganic molecular layer deposition (MLD) films under inert atmosphere. This method is general and has been applied to form TiO_2/C , $\text{Al}_2\text{O}_3/\text{C}$, ZnO/C , ZrO_2/C and HfO_2/C composite films from titanocene, alucone, zincone, zircone and hafniconce MLD films, respectively. Most of the work has focused on TiO_2/C and $\text{Al}_2\text{O}_3/\text{C}$ composite films. Raman measurements have observed the growth of the signature D and G peaks of graphitic carbon after pyrolysis under argon at $\geq 600^\circ\text{C}$. The sheet resistance of the pyrolyzed MLD films also decreased by orders of magnitude with increasing pyrolysis temperature. Minimum sheet resistances were obtained for titanocene and alucone MLD films after pyrolysis at 800 and 850°C , respectively. The ability to coat conformally high aspect ratio electrodes with hybrid organic-inorganic MLD films and then pyrolyze these MLD films to obtain conducting metal oxide/carbon composite films will have many important applications in electrochemistry. Possible areas include Li ion batteries and pseudocapacitance supercapacitors.

4:40pm TF+AS+SE+SS-MoA9 Molecular Layer Deposition of Organic-Inorganic Hybrid Materials for Implant BARC Applications, L.N.J. Rodriguez, C. Adelmann, B. Sutens, G. Winroth, A. Delabie, R. Gronheid, S. Van Elshocht, IMEC, Belgium

Molecular Layer Deposition (MLD), a variant of Atomic Layer Deposition (ALD) whereby organic groups are used to link the metal atoms within the growing film can create films with optical properties which are unreachable by ALD alone. The ability to make highly conformal films of specified thickness and optical properties should be of use in supplying Bottom Anti-Reflective Coatings (BARC) for lithography processes. The advantage lies in finely tuned patterning control, minimising etch damage to the underlying topography in applications such as ion implantation masking. Optical simulations were performed for a 110nm trench using 193nm exposure at 0.85NA with conventional illumination and with the MLD thickness of 5nm and having $n=1.4$ and $k=0.8$, in order to validate this approach. The growth rate of alucones by MLD was highly dependent on the temperature but did show self-limiting growth. While the refractive index of the alucones is lowered towards the target region, the absorption constant was too low. Therefore the ethylene glycol in the MLD was replaced with aromatic precursors so as to increase the optical absorption of the films. The conformality of the films was tested with fin structures and the process developed for transfer from coupons to full wafers.

5:00pm TF+AS+SE+SS-MoA10 Mechanical Property Modification of Fiber Forming Polymers by Sequential Organometallic Exposures, R.P. Padbury, J.S. Jur, North Carolina State University

Hybrid organic-inorganic materials are of increasing interest in the development of novel materials that unite characteristic properties of both

organic and inorganic constituents. This work explores the infiltration of ALD precursors into fiber forming polymers and the subsequent formation of a hybrid material interface. The hybrid functionalization is formed as a result of precursor diffusion through the porous sub-surface of the organic material which is followed by chemical reaction and nucleation. Previous research exploring the infiltration of organometallic precursors into polyamide-6 (PA-6) films via in-situ quartz crystal microgravimetry (QCM) indicates a strong dependence on the glass transition temperature of the polymer film. To explore this in more detail, in-situ QCM is employed to investigate the infiltration behavior of a series of polyesters and polymethacrylates that possess variations in functional group concentration and glass transition temperatures. The effect of this processing on the mechanical behavior of fibrous materials is also investigated. In particular this report highlights the structure-process-property relationships between modified and unmodified polyester fibers that have been infiltrated with trimethylaluminum (TMA). The results indicate that as the number of TMA cycles increases the peak load and elongation of the single fiber also increases. Mechanical testing is complemented by ex-situ characterization methods such as TEM to examine the interaction between the precursor and polymer and the composition of the hybrid layer. This work has important implications on sustainable textiles processes as well as the introduction of hybrid material properties to polymer systems.

5:20pm TF+AS+SE+SS-MoA11 Vapor-Phase Modification of Simple Sugars Towards New Hybrid Organic-Inorganic Materials, K. Gregorczyk, L. Zhang, M. Knez, CIC nanoGUNE, Spain

The incorporation of transition metals into organic materials has lead to a variety of unusual or improved physical and chemical properties. Of particular interest is the use of inexpensive biological materials as substrates or scaffolds due to their naturally occurring, and often complex, morphologies. For simple coatings atomic layer deposition (ALD) has been proven to be the technique of choice due to its low reaction temperatures, monolayer thickness control, and extreme conformality. Furthermore, recent modifications to this technique have allowed infiltration of the metal-organic precursors into a variety of organic materials including spider silk[1], porphyrins [2], and polytetrafluoroethylene (PTFE)[3], leading to a more detailed understanding of the reaction between these organic substrates and the metal-organic precursors. Using this technique, we present work studying the interaction of trimethyl aluminum and diethyl zinc with simple sugar molecules (monomers, dimers, and polymers). We report chemical and mechanical modifications to the simple monosaccharide glucose, the polysaccharide sucrose, and the polymer cellulose. Reaction detail differences between the simple monomer molecules (glucose) and their corresponding polymers (cellulose) will be discussed though mass spectrometry, Raman spectroscopy, and UV-vis. Mechanical and chemical changes to these materials will also be presented.

1. Lee, SM *et al.* Science, **324**, 488 (2009)
2. Zhang, L, *et al.* Angew. Chem. Int. Ed., **48** (2009)
3. Lee, SM, *et al.* Adv. Funct. Mater., **21** (2011)

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