Tuesday Afternoon, October 19, 2010

Thin Film
Room: Ruidoso - Session TF-TuA

ALD/CVD: Surface Chemistry and Fundamentals
Moderator: S.M. Rossnagel, IBM Research

2:00pm TF-TuA1 Studying Roll-to-Roll ALD Process Conditions Using a Moving Substrate Under a Gas Source Coating Head, *R. Fitzpatrick, Z.M. Gibbs, S.M. George*, University of Colorado
Continuous roll-to-roll ALD processing is currently being developed for economical and efficient ALD on polymer and other flexible substrates. One of the key implementations of roll-to-roll ALD was introduced by Kodak (D. H. Levy et al., *Appl. Phys. Lett.* **92**, 192101(2008)). To understand the dependence of roll-to-roll ALD on process conditions, we have constructed a laboratory-scale apparatus featuring a fixed gas source coating head that sits in ambient above a moving substrate that is driven by a programmable stepper motor. The gas source coating head consists of a series of rectangular channels that spatially separate the ALD reactions. As the substrate moves under the gas source coating head, the channel sequence for each reactant is: precursor; exhaust; N_2 purge; and exhaust. The gas source head was built for 1.5 ALD cycles. Using Al_2O_3 ALD as a model system, the gas source head has the trimethylaluminum (TMA) channel sequence in the middle and the water channel sequence on each side of the TMA. This design allows for the deposition of two Al_2O_3 ALD cycles during one complete back-and-forth translation of the moving substrate. A low conductance gap between the precursor and exhaust channels allows for nearly "static" reactant exposures and prevents intermixing of the reactants. A higher conductance gap was machined into the gas source head between the exhaust and purge channels to create a "high flow" entrainment region that further isolates the precursor channels. The spacing between the gas source head and substrate is fixed and can be controlled with micron precision. This new apparatus can test how roll-to-roll ALD depends on the gap spacing, substrate speed, gas flow rates, and pressure difference between reactant and purge channels. An understanding of these process parameters will be necessary for the successful implementation of continuous, large scale roll-to-roll ALD.

2:20pm TF-TuA2 Reactive Intermediates during Atomic Layer Deposition of Aluminum Oxide from Ozone and an Oxygen Plasma, *V.R. Rai*, Colorado School of Mines, *V. Vandalon*, Eindhoven University of Technology, Netherlands, *S. Agarwal*, Colorado School of Mines
In this presentation, the authors will elucidate the surface reaction mechanisms during the atomic layer deposition (ALD) of aluminum oxide from trimethyl aluminum (TMA) in conjunction with O_3 and an O_2 plasma. The deposition mechanism was explored over a substrate temperature range of 70–200 °C using in situ attenuated total reflection Fourier transform infrared spectroscopy. Our IR data show that both –OH groups and carbonates are formed on the surface during the oxidation cycle. Gas-phase IR data indicate that oxidizer-assisted combustion of methyl ligands in chemisorbed TMA produces CO_2 and H_2O, which react simultaneously on the Al_2O_3 surface to produce carbonates. The origin of the –OH groups was attributed to the reaction of the uncombusted methyl ligands with gas-phase H_2O. While the type of surface sites are common to both oxidizing agents, in the case of O_2-plasma-assiated ALD, surface carbonates are simply reactive intermediates, which completely decompose upon prolonged plasma exposure. The ratio of carbonates to –OH groups is strongly dependent on the oxidizing agent, and its dose in case of plasma-assisted ALD. Surface reactions such as chemisoption of TMA, formation of –OH groups and Al_2O_3 were pseudo first order. On the other hand, the kinetic behavior of the carbonates suggests a series reaction of the type, A (CH_3) → B (carbonates) → C (Al_2O_3). Although carbonate sites contribute to Al_2O_3 growth, their contribution was determined to be insignificant.

2:40pm TF-TuA3 Synthesis of Micro/Mesoporous Alumina Fibers by Gas Phase Infiltration of Polyesters with Trimethyl Aluminum and Water, *B. Gong, Q. Peng, C. Devine, K. Lee, G.N. Parsons*, North Carolina State University
Preparation of inorganic micro/mesoporous materials has attracted considerable attention because of their function in catalytic, separations, and other applications. Although many approaches are known to synthesize porous materials, methods to form mesoporous materials with pre-determined shape and morphology are not readily known. Sub-surface deposition, recently observed during atomic layer deposition (ALD) on polymer substrates, provides a potential method to transform polymers from fully organic solids into organic-inorganic hybrid and micro/mesoporous

materials. Moreover, the transformation allows polymers with well defined micro and nano-structure, such as polymer fiber matrices, to maintain their shape and structure to form new replica materials. In this presented work, we apply this process to synthesis of Al-O/organic hybrid micro fibers by gas phase infiltration of tri-methyl aluminum and water alternatively into polyesters, such as polybutylene terephthalate (PBT). Through in-situ infrared analysis, we show that TMA acts as a strong Lewis acid and attacks the nucleophilic ester groups in polyesters to insert Al-O bonds into the polymer chains. The organic components are removed by post annealing to produce a micro/mesoporous alumina fiber. Surface area, pore volume, and pore size distribution of the porous alumina fibers were tested by nitrogen adsorption/desorption experiments, and surface areas exceeding 400 m^2/g were obtained. SEM was used to track the morphology change along the process, and cross-section TEM images of annealed samples confirmed the formation of porous structures.

3:00pm TF-TuA4 Growth Rate Control in ALD by Surface Functionalization: Alkyl Alcohols on Metal Oxides, *A. Yanguas-Gil, J.W. Elam*, Argonne National Laboratory
In this work we explore the effect that alkyl alcohols (ROH) have on the saturation growth rate during the ALD of metal oxides. The traditional dosing sequence for metal oxide ALD is: M/O/M/O… where M is the metal precursor and O is the oxygen source. We find that by dosing organic molecules prior to dosing the metal precursor (e.g. ROH/M/O…) we can modify the surface chemistry and control the saturation growth rate. We will present results describing the effect of alkyl alcohols (R=Me, Et, iPr, and Bu) using H_2O as the oxygen source and the metal precursors $Ti(iPr)_4$ for TiO_2 ALD, TMA for Al_2O_3 ALD, and DEZ for ZnO ALD. Furthermore, we demonstrate this effect in the ALD of doped metal oxides.

Our results show that the ROH/M/H_2O sequence causes a substantial reduction in the growth per cycle for all of the ALD systems studied. For instance, the growth per cycle reduces from 0.31 to 0.06 Å/cycle in the case of TiO_2 ALD using MeOH/$Ti(iPr)_4$/H_2O, and from 1.2 to 0.4 Å/cycle in the case of Al_2O_3 ALD using MeOH/TMA/H_2O at 200°C.

Previous studies in the literature indicate that ROH reacts with basic sites on the metal oxide surface. Alcohol deprotonation followed by metal oxygen heterolytic bond formation leads to the formation of alkoxide functional groups bound to metal cations. To investigate this process, we performed *in situ* mass spectrometry and quartz crystal microbalance studies during the ROH/M/H_2O dosing sequence. We discovered that the ROH adsorbed on the surface desorbs intact as ROH during the subsequent water pulse, but no alcohol is released during the metal precursor pulse. Furthermore, the reduction of the growth rate per cycle is not affected by purge times, suggesting that the ROH molecules bond strongly to the metal oxide surface. Finally, no reduction in growth per cycle is observed using the dosing sequence: ROH/H_2O/TMA/H_2O. This finding suggests that the ROH and H_2O are able to displace one another, and signifies an almost complete elimination of the alkoxide groups during the water pulse. This observation agrees with the many reports of successful metal oxide ALD using metal alkoxide and water.

The ability to tune the saturation growth rate by modifying the surface chemistry can be of great utility for the ALD of doped materials where a homogenous distribution of dopants at a low concentration is desired.

4:00pm TF-TuA7 , *V.R. Anderson, A.S. Cavanagh, A.I. Abdulagatov, Z.M. Gibbs, S.M. George*, University of Colorado
Most processes for TiO_2 atomic layer deposition (ALD) utilize water or other oxidants that can oxidize some substrates of interest. To avoid this oxidation, waterless or oxidant-free surface chemistry can be used that involves titanium halides and titanium alkoxides. This waterless surface chemistry approach for metal oxide ALD was originally proposed by the University of Helsinki group (M. Ritala et al., *Science* **288**, 319 (2000)). In this study, TiO_2 ALD was accomplished using titanium tetrachloride ($TiCl_4$) and titanium tetraisopropoxide (TTIP). In situ Fourier transform infrared (FTIR) studies revealed that the mechanism for TiO_2 ALD using $TiCl_4$ and TTIP changed with temperature. At high temperatures between 250 and 300 ºC, the isopropoxide species after TTIP exposures quickly underwent beta-hydride elimination to produce TiOH species on the surface. The observation of propene by quadrupole mass spectrometry confirmed the beta-hydride elimination reaction pathway. The $TiCl_4$ exposure then reacted with the TiOH species to deposit $TiCl_x$ species on the surface. At low temperatures between 125 and 200 ºC, the isopropoxide species remained after TTIP exposures to react with $TiCl_4$. However, this reaction was much less efficient than the reaction of $TiCl_4$ with TiOH species. Quartz crystal microbalance (QCM) studies were also used to monitor TiO_2 ALD at low and high temperatures. The QCM studies measured low TiO_2 growth rates

of ~3 ng/cm^2 at a low temperature of 150°C. In contrast, much higher TiO$_2$ growth of ~15 ng/cm^2 were observed at a higher temperature of 250°C under similar reaction conditions. X-Ray reflectivity measurements determined that TiO$_2$ ALD using TiCl$_4$ and TTIP at 250°C produced a growth rate of 0.5-0.6 Å per cycle. X-Ray photoelectron studies also confirmed TiO$_2$ film growth with a chlorine contamination of less than 0.5 at%. This waterless TiO$_2$ ALD process using TiCl$_4$ and TTIP should be valuable for preventing substrate oxidation during TiO$_2$ ALD on oxygen-sensitive substrates such as cobalt.

4:20pm TF-TuA8 Growth Mechanism and Properties of Mg$_x$Zn$_{(1-x)}$O Nanocomposites by Atomic Layer Deposition, *Q. Peng, A.U. Mane, J.W. Elam*, Argonne National Laboratory

Magnesium-zinc oxide (Mg$_x$Zn$_{(1-x)}$O) ternary films are an interesting class of alloy materials in which the band gap can be tuned by adjusting the Mg doping concentration. Consequently, Mg$_x$Zn$_{(1-x)}$O has been widely studied for application in the fields such as electronics, optics, photoelectronics, and solar cells. Mg$_x$Zn$_{(1-x)}$O thin films have been fabricated through a variety of methods including chemical vapor deposition, physical vapor deposition, molecular beam deposition, and ALD. Although there have recently been a few reports describing ALD Mg$_x$Zn$_{(1-x)}$O for application in photvtolaics, there has been no detailed study of the growth mechanism and properties of the ALD Mg$_x$Zn$_{(1-x)}$O thin films.

In this work, the ALD Mg$_x$Zn$_{(1-x)}$O was systematically explored with different doping concentration of Mg by using diethyl zinc (DEZ), bis-cyclopentadienyl-magnesium (Cp$_2$Mg) and H$_2$O as the precursors. The growth mechanism was investigated using quartz crystal microbalance and quadrupole mass spectrometry measurements. The growth rate of the Mg$_x$Zn$_{(1-x)}$O alloy films was determined using spectroscopic ellipsometry. The crystal structures of the films before and after thermal treatment were analyzed using x-ray diffraction. In addition, the optical properties of the Mg$_x$Zn$_{(1-x)}$O with different Mg concentrations were analyzed using UV-vis absorption spectroscopy and the electrical properties were evaluated using mercury probe current-voltage measurements. The thermal stability of the conductivity and structure of the Mg$_x$Zn$_{(1-x)}$O films were studied as well. The system will be compared with Al doped ZnO system fabricated by ALD, to illustrate the conduction mechanism in doped ZnO synthesized by ALD process.

4:40pm TF-TuA9 Nucleation and Growth of Conformal and Ultrathin Pt Films on Al$_2$O$_3$ and W Substrates Using Plasma Enhanced ALD, *L. Baker, A.S. Cavanaugh, D. Seghete, S.M. George*, University of Colorado, *A.J.M. Mackus, E.W.M.M. Kessels*, Eindhoven University of Technology, Netherlands, *Z.Y. Liu, F.T. Wagner*, General Motors Research & Development

Pt ALD using thermal chemistry has nucleation difficulties and leads to the deposition of Pt nanoclusters. In contrast, Pt ALD using O$_2$ plasma nucleates much more readily and spectroscopic ellipsometry (SE) studies are consistent with continuous Pt films (H.C.M. Knoops et al., *Electrochem. Solid-State Lett.* 12, G34 (2009)). However, SE measurements alone were insufficient to characterize the early stages of the Pt ALD process. In this investigation, we have examined Pt ALD with MeCpPtMe$_3$ and O$_2$ plasma as the reactants using SE, X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) studies versus the number of ALD cycles. Analysis of the XRR and XPS results indicates that plasma Pt ALD on Al$_2$O$_3$ ALD substrates has a short nucleation delay. The nucleation delay is followed by a brief period of rapid Pt ALD film growth of 0.1 nm per cycle that is followed by a slower steady-state Pt ALD film growth of ~0.05 nm per cycle. During the Pt ALD nucleation and growth on the Al$_2$O$_3$ ALD substrate, SEM images show that the Pt film morphology evolves from isolated nanoclusters to worm-like nanostructures and finally to a conformal film at a Pt film thickness of approximately 7 nm. Nucleation and growth of Pt ALD on W ALD substrates led to very different results. In this case, a H$_2$ plasma was used instead of an O$_2$ plasma to prevent oxidation of the W ALD substrate. XRR and XPS studies revealed that Pt ALD with MeCpPtMe$_3$ and H$_2$ plasma as the reactants on W ALD substrates nucleated immediately and a continuous and conformal Pt ALD film was formed at a Pt ALD thickness of less than 5 nm. These results indicate that Pt ALD can be tuned to produce Pt nanoclusters or a continuous and conformal ultrathin Pt film using either thermal or plasma Pt ALD.

5:00pm TF-TuA10 Homogeneous Thermal Decomposition of Triethylaluminum: Effect of NH$_3$, *J. Lee, T.J. Anderson*, University of Florida

Thermal decomposition pathways of triethylaluminum ((C$_2$H$_5$)$_3$Al, TEAl) were investigated in a custom, up-flow, cold-wall CVD reactor . The extent of homogeneous decomposition of TEAl in N$_2$ as well as with added NH$_3$ was measured using *in situ* Raman spectroscopy measurement. The results

of Density Functional Theory (DFT) calculations were used to assist in assignment of the observed Raman shifts to the decomposition products TEAl:NH$_3$, DEAlH, TEAl:NH$_3$ H$_2$N-AlH-NH-AlH$_2$, H$_2$Al-NH$_2$, MEAlH, MEAlH-AlH$_2$ and DEAl-AlH$_2$ as well as the estimating the rates of selected pathways. For the case of thermal decomposition of TEAl with N$_2$ carrier gas, the species H$_2$Al–NH$_2$ was observed . This is believed to result from the reaction of ammonia with the product of β–hydride elimination. This species is a possible reactant for AlN formation. Raman shifts of 600, 1989, 2025, 2580, 2835, 2849, 2900, 2918, 2939, and 3173 cm^{-1} were recorded for TEAl in N$_2$, while shifts of 452, 1462, 1525, 1639, 2580, 2853, 2841, and 2849 cm^{-1} were observed for a mixture of TEAl with ammonia in N$_2$. In addition, four vibrational bands (930, 965, 3230, and 3334 cm^{-1}) for ammonia were observed with high intensity. The temperature profile along the reactor centerline was measured and this was compared to the simulated results using a custom-FEM Galerkin method. DFT calculations using B3LYP/LanL2DZ level of theory were carried out to find the optimized geometry of each intermediate and transition structure and to calculate activation energy. This methodology, which uses the results from *in situ* Raman spectroscopy, DFT calculations, and FEM reactor modeling, is a powerful approach to understanding thermal decomposition mechanisms.

5:20pm TF-TuA11 Surface Reactions of TiCl$_4$ and Al(CH$_3$)$_3$ on GaAs(100), *B. Granados, A.J. Muscat*, University of Arizona

5:40pm TF-TuA12 Atomic Layer Deposition of Co-Al Films Studied by In-Situ Infrared Spectroscopy, *J. Kwon, Y.J. Chabal,* University of Texas at Dallas, *J. Anthis, R. Kanjolia*, SAFC Hitech

Cobalt-aluminum alloys are of great interest due to their unique properties such as corrosion resistance, high thermal stability, and unusual magnetic properties. In a search for appropriate precursors, we have investigated the growth of Co-Al thin films by atomic layer deposition (ALD) using CCTBA (μ^2-h^2-(^{t}Buacetylene)dicobalthexacarbonyl) and DMAH (Dimethylaluminumhydride) on H-terminated Si(111) and on 2-nm TaN films. In-situ infrared absorbance spectra show that upon the first CCTBA pulse on H/Si(111), alkynes (CC triple bonds) bound to Co$_2$(CO)$_6$ are converted to a benzene ring, as evidenced by the ring C=C stretching mode at 1475 and 1610 cm^{-1}. This transformation is not completely unexpected because cobalt carbonyl complexes (Co$_x$(CO)$_y$) are used to catalyze cyclotrimerization reactions in organotransition-metal chemistry. IR spectra also show that the presence of hydrogen enhances the adsorption of carbonyl groups on the H/Si(111) surface. After the first CCTBA pulse which reacts almost completely with H–Si bonds (2083 cm^{-1}), the amount of adsorbed CO on the surface (1970 cm^{-1}) is found to decrease. The subsequent DMAH pulse is effective to remove the surface carbonyl groups, leaving Al–CH$_3$ and/or Al–H bonds on the surface. In contrast, the adsorption of carbonyl on a TaN surface where H is absent is negligible after the first CCTBA pulse.

In all cases, CH$_x$ ligands are not removed during CCTBA or DMAH cycles, leading to accumulation of carbon species in the film. The growth of metallic Co-Al films is hindered due to Al–O bond formation during deposition. The source of oxygen is likely associated to a surface Fischer-Tropsch (FT) process. It appears that reaction of cobalt particles with hydrogen (originating from the DMAH precursor) generates water as a by-product through a FT-like process, thus forming Al–O bonds. This formation of Al-O bonds through a FT process is greatly suppressed (~ 50%) by annealing the sample to 300 °C in N$_2$ ambient before exposure to DMAH, which removes the carbonyl group from the surface and therefore the source of oxygen. Although the growth pattern is similar for both H/Si(111) and TaN substrates, a part of Ta atoms in the original TaN films are reduced to metallic Ta^0 during growth, according to XPS Ta 4f core level spectrum after deposition of Co-Al(O$_x$) films.

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