Monday Afternoon, October 20, 2008

Thin Film
Room: 302 - Session TF-MoA

ALD: Functionalization and Surface Chemistry
Moderator: R.G. Gordon, Harvard University

2:00pm TF-MoA1 Atomic Layer Deposition of Platinum on Strontium Titanate Surfaces, *J.W. Elam*, Argonne National Lab., *S.T. Christensen, F.A. Rabufetti*, Northwestern U., *W. Setthapun, B. Lee*, Argonne National Lab., *Z. Feng*, Northwestern U., *P.C. Stair*, Argonne National Lab. & Northwestern U., *C.L. Marshall*, Argonne National Lab., *K.R. Poeppelmeier*, Northwestern U., *M.J. Bedzyk*, Argonne National Lab. & Northwestern U., *M.C. Hersam*, Northwestern U.

Platinum supported on metal oxide surfaces has important technological applications in oxidative dehydrogenation catalysis, photocatalysis, and in catalytic converters. The atomic layer deposition (ALD) of Pt on oxide surfaces is unusual because it proceeds via nucleation, growth and coalescence of islands in contrast to the layer-by-layer behavior typically observed during the ALD of metal oxides. This natural tendency towards agglomeration combined with the ability to infiltrate porous materials makes ALD Pt an attractive method for preparing catalysts on high surface area supports. In this presentation, I will describe our recent work exploring Pt ALD on strontium titanate (STO) surfaces including both single crystal STO(001) substrates as well as novel STO nanocubes prepared by hydrothermal methods. We use a broad variety of methods to characterize these samples including atomic force microscopy, scanning- and transmission-electron microscopy, grazing incidence small angle X-ray scattering, X-ray reflectivity, X-ray fluorescence, and extended X-ray absorption fine structure measurements. These ex situ measurements are complemented by in situ quartz crystal microbalance and quadrupole mass spectrometer studies examining the mechanism of Pt ALD. These measurements clearly reveal the nucleation and growth of nm-sized Pt clusters on the STO surfaces where the Pt cluster size is controlled by the number of Pt ALD cycles. These Pt clusters are remarkably active for catalyzing the oxidation of hydrocarbons as demonstrated by propane light-off studies. The Pt clusters are very stable on the STO surfaces at temperatures up to 400-500°C, but sinter when heated to 800°C in vacuum.

2:20pm TF-MoA2 Remote Plasma and Thermal ALD of Platinum and Platinum Oxide Films, *W.M.M. Kessels, H.C.M. Knoops, A.J.M. Mackus, S.A.F. Dielissen, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Due to its chemical stability and excellent electrical properties platinum has wide application prospects in catalysis and microelectronics. Recently the deposition of Pt films in complex 3D structures by ALD has gained interest for catalyst applications in fuel cells and as a current collector layer in Si-integrated solid-state thin film Li-ion batteries. In this contribution we report on thermal and remote plasma ALD of Pt films using $MeCpPtMe_3$ precursor combined with O_2 gas and O_2 plasma, respectively. For the thermal process the results obtained by Aaltonen et al.[1] were reproduced (growth per cycle is 0.045±0.005 nm) and special attention was given in characterizing the growth incubation period on Si with thermal and native oxide by using in situ spectroscopic ellipsometry. With the new remote plasma ALD process (growth per cycle is 0.047±0.005 nm) the growth incubation could be reduced to a few cycles yielding the possibility to initialize Pt growth by depositing a remote plasma ALD "seed layer" and thickening the film by thermal ALD. A short plasma exposure (0.5 s) was necessary to deposit Pt films with no detectable amount of oxygen while a long O_2 plasma exposure (5 s) resulted in platinum dioxide ($PtO_{2.2}$, growth per cycle is 0.048±0.004 nm). Pt films were deposited with a mass density of 20.8 g/cm^3 and an electrical resistivity of 14 $\mu\Omega$ cm, both close to the bulk values of 21.4 g/cm^3 and 10.8 $\mu\Omega$ cm. The platinum oxide films had a mass density of 8.9 g/cm^3 and they showed a semi-conductive behavior (resistivity of >100 Ω cm, bandgap 0.85 eV). In addition to ex situ film analysis, several in situ diagnostics have been employed. With spectroscopic ellipsometry the film thickness and (optical) film properties were monitored as a function of the number of cycles. From the Drude parameters in the Drude-Lorentz optical parameterization of the platinum, information about mass density and electrical resistivity was extracted. With infrared transmission spectroscopy the consumption of $MeCpPtMe_3$ precursor was measured while currently also the reaction products generated during the surface reactions are being investigated.

[1] T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskela, Chem. Mater. 15, 1924 (2003).

2:40pm TF-MoA3 Growth Kinetics and Mechanism of Rapid SiO_2 ALD Using Tris(tert-Pentoxy)Silanol, *S.M. George*, B.B. Burton, University of Colorado

Rapid SiO_2 ALD can deposit very thick, ~100 Å, conformal SiO_2 films by exposure of various silanol precursors to surfaces covered with Al-catalysts. Rapid SiO_2 ALD with tris(tert-butoxy)silanol (TBS) was reported at temperatures from 200−300°C and deposited SiO_2 film thicknesses as large as 120 Å [R.G. Gordon and coworkers (Science 298, 402 (2002)]. In this study, we have explored the growth of rapid SiO_2 ALD films using liquid tris(tert-pentoxy)silanol (TPS). TPS can deposit even thicker SiO_2 films at lower temperatures. The rapid SiO_2 ALD growth is believed to result from the growth of siloxane polymer chains at Al-catalytic sites and the cross-linking of these polymer chains to form a dense SiO_2 film. The SiO_2 film thicknesses deposited during one silanol exposure are dependent on the temperature, silanol pressure, and silanol exposure time. SiO_2 film thicknesses were determined using quartz crystal microbalance and x-ray reflectivity measurements. For TPS exposures of 1 second, the SiO_2 ALD growth rate was larger at lower temperatures and larger TPS pressures. SiO_2 ALD thicknesses of 125−140 Å were observed at the highest TPS pressures of ~1 Torr at the lower temperatures. These results indicated that higher TPS fluxes increase the siloxane polymerization rates. Likewise, the lower temperatures reduce the cross-linking rates between the siloxane polymers that self-limits the SiO_2 deposition. To explore the rate of cross-linking between the siloxane polymers, experiments were conducted where small TPS micropulses were employed with different delay times between the micropulses. The final limiting SiO_2 ALD mass gains decreased with increasing delay times. This behavior suggested that the longer delay times produced more cross-linking that self-limits the SiO_2 deposition. Other experiments showed that higher temperatures produced faster nucleation of the rapid SiO_2 ALD. The nucleation was nearly immediate at the higher temperatures and could be as long as 10 seconds at the lower temperatures. The growth kinetics of rapid SiO_2 ALD can be understood in terms of the temperature dependence of nucleation and cross-linking and the pressure dependence of the siloxane polymerization rate.

3:00pm TF-MoA4 Atomic Layer Deposition of Titanium Dioxide: Reaction Mechanism Studies using In Situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy, *V.R. Rai*, S. Agarwal, Colorado School of Mines

The authors have investigated the surface reaction mechanism during the atomic layer deposition (ALD) of TiO_2 using titanium tetraisopropoxide (TTIP) as the metal precursor and O_3, atomic O, and H_2O as the oxidizers. The surface species during each half-reaction cycle were detected using in situ, real-time attenuated total reflection Fourier-transform infrared spectroscopy. Sub-monolayer sensitivity was obtained by multiple internal reflections through the ZnSe internal reflection crystal, which has a refractive index that is closely matched to that of amorphous TiO_2. We find that the surface reaction mechanism is very different for O_3- and H_2O-based ALD. Surface hydroxyl groups are generally the reactive sites for the metal precursors in a H_2O-based ALD process. In contrast, we do not detect any hydroxyl groups on the surface after the O_3 cycle. Our data shows that the reactive sites for the adsorption of TTIP after O_3 exposure of the surface are carbonate groups with symmetric and anti-symmetric stretching absorptions in the 1400 − 1700 cm^{-1} region. These surface carbonates can be present as mono-, bi-, or poly-dentates. Due to their thermal stability at the growth temperature, all three types of carbonated are present simultaneously resulting in several overlapping absorption bands in the 1400 − 1700 cm^{-1} region, which could not be deconvoluted. We hypothesize that during O_3 exposure, CO_2 and H_2O are formed due to the combustion of isopropoxy ligands and a small fraction of these molecules react with the TiO_2 surface producing these surface carbonates. CO_2 was in fact detected as one of the reaction products in the gas-phase by the IR beam passing through the chamber. When the isopropoxy ligands react with the surface, CO_2 from the carbonates was released into the gas phase and was again detected by the IR beam. Using O_3 as the oxidizer, relatively contaminant-free TiO_2 films were deposited at 150 °C: this is nearly 100 °C lower than the widely-accepted minimum temperature for the TTIP-H_2O ALD window. Ex situ spectroscopic ellipsometry data shows a refractive index of ~2.2 and a nearly constant growth rate of ~0.52 Å/cycle over the temperature range of 150-250 °C.

3:20pm TF-MoA5 Surface Preparation and Interface Cleaning during HfO_2 ALD on GaAs, *T. Gougousi*, J.C. Hackley, UMBC, *J.D. Demaree*, Army Research Laboratory

The atomic layer deposition of HfO_2 thin films is studied on GaAs(100) surfaces. The films are grown using tetrakis(dimethyl)amino hafnium

(TDMAH) and H_2O precursors at a deposition temperature of 275°C. Several GaAs starting surfaces are investigated, including native oxide and both HF and NH_4OH-treated substrates. Wet chemical etching in either HF or NH_4OH solutions are shown to remove most of the Ga and As native oxides. Spectroscopic ellipsometry (SE) confirms linear growth rates of ~1.0 Å/cycle for all surfaces. Rutherford backscattering spectrometry (RBS) shows that steady-state growth of 2.6×10^{14} $Hf/cm^2/cycle$ is reached after 10 ALD cycles for the HF-etched GaAs surface while much smoother growth is observed for the native oxide surface (~2.9×10^{14} $Hf/cm^2/cycle$). The interface of HfO_2 films deposited on GaAs surfaces is probed by X-ray photoelectron spectroscopy. Both the HF and NH_4OH treatments passivate the surface and prevent the oxidation of the interface during the deposition of coalesced HfO_2 films (> 15 ALD cycles). Deposition of HfO_2 films on the native oxide GaAs surfaces show gradual consumption of the native oxides during the process, indicating the presence of an "interfacial cleaning" mechanism comparable to that observed for other metal oxide ALD processes on GaAs and InGaAs substrates.[1,2,3,4] The As-oxide and most of the Ga-oxide is removed after 20 ALD cycles. The presence of As oxides is not detected for films as thick as ~100Å (100 cycles) deposited on native oxide substrates.

[1] M.M. Frank, G.D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y.J. Chabal, J. Grazul, D.A. Muller, Appl. Phys. Lett. 86, 152904 (2005)
[2] M.L. Huang, Y.C. Chang, C.H. Chang, Y.J. Lee, P. Chang, J. Kwo, T.B. Wu, M. Hong, Appl. Phys. Lett. 87, 252104 (2005)
[3] C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, J. Kwo, Appl. Phys. Lett. 89, 242911 (2006)
[4] D. Shahrjerdi, E. Tutuc, S.K. Banerjee, Appl. Phys. Lett. 91, 063501 (2007).

4:00pm TF-MoA7 New Barium, Strontium, and Titanium Precursors for the Deposition of Barium/Strontium-containing and Titanium Nitride Thin Films, *Q.M. Wang, D.V. Shenai,* Rohm and Haas Electronic Materials LLC, *R.G. Gordon,* Harvard University

Atomic Layer Deposition (ALD) is a technology gaining recognition in the semiconductor industry because of its exceptional benefits: an extremely precise thickness control, a very good composition control, an excellent conformality over aggressive geometries, and a wide deposition temperature window. As a result, numerous ALD-based processes are currently being developed for depositing a wide variety of metals and dielectrics for high-k gate dielectrics, metal gate/capacitor electrodes, barrier metals, seed layers, and ferroelectric films. Identification of suitable precursors has often been one of the challenges and critical success factors in ALD process development. The thermal stability and vapor pressure of the sources play a significant role in the stringent selection criteria along with a high reactivity with the second reactant in a wide temperature window, an acceptable shelf-life, and an ultra-high purity. For the ALD of high-k dielectrics, metal halides were adopted early on as the precursors of choice, which were later replaced by metalorganic sources with metal-nitrogen bonds such as metal dialkylamides and more recently developed metal amidinates. The metal amidinate sources have produced excellent results in the deposition of many thin film materials. In this study, we report the synthesis of new dialkylamidinate precursors for barium, strontium and titanium. These amidinate complexes display high thermal stabilities, acceptable vapor pressures and promise to be superior sources for deposition of barium/strontium-containing titanate, niobate, or tantalate thin films, as well as titanium nitride films by ALD. Volatility and thermal stability data for the barium, strontium and titanium amidinate complexes will be discussed. The barium and strontium amidinates are dimeric crystalline materials. The new titanium(III) amidinate is a low-melting material that greatly facilitates its handling in bubblers, while the titanium(IV) amidinate is a dimeric crystalline material. Data showing the high purity of the amidinate sources will be demonstrated by ICP-MS and FT-NMR analysis, and data characterizing their thermal stabilities will be provided from TGA/DSC and FT-NMR analysis. Preliminary deposition results of barium titanate, strontium titanate, and barium-strontium titanate thin films with these amidinate precursors will be provided.

4:20pm TF-MoA8 Ab Initio and FTIR Study of TDMAH and HTB Adsorption and Reaction on Hydrogen-terminated Si Surfaces, *K. Li*, N. Li, H.C. Turner, T.M. Klein, University of Alabama

An ab initio study of the reaction pathway and energetics of HfO2 deposition from tetrakisdimethylamido hafnium (TDMAH) and hafnium tert-butoxide (HTB) onto hydrogen terminated Si(111) and Si(100) is compared with ATR-FTIR experimental data between 330K and 520K. Hf-OH streching modes are evident at low temperatures for the HTB reaction while Hf-H streching modes are predominant for TDMAH chemisorbed layers. A mechanism involving silyl radicals for the later is proposed. The results are important towards understanding the limitations of atomic layer deposition during the initial growth phase. Factors influencing the interface bonding and coverage limitation will be discussed.

4:40pm TF-MoA9 In-situ Quadrupole Mass Spectroscopy Analysis of Low Temperature Cobalt Deposition Reactions using $Co_2(CO)_8$ and $Co(C_5H_5)(CO)_2$ in Atomic Layer Deposition Process Sequencing, *S.J. Oh, G.N. Parsons*, North Carolina State University

Cobalt is of interest as a catalyst in Fisher-Tropsch synthesis, in the Pauson–Khand reaction and for carbon nanotube growth. Cobalt's high magnetic permittivity also makes it valuable for data storage applications. Cobalt thin films are widely deposited by thermal and plasma ALD and CVD at temperatures between 200 and 400 °C. Lower temperature deposition processes are beginning to open new applications, including coating of temperature sensitive polymers and templating of biological materials. However, processes for conformal metal film deposition at less than 150 °C are not widely available. Previous studies of CVD Co from $Co_2(CO)_8$ show a transition in reaction kinetics at temperatures near 100 - 150 °C, consistent with a thermally activated increase in gas phase interactions between precursor molecules resulting in a decrease in deposition rate with increasing temperature. For this work, we undertook a study of low temperature cobalt thin film deposition using ALD process sequencing under the hypothesis that avoiding precursor interactions may produce a viable low temperature ALD process. Film growth was studied between 30 and 130 °C using $Co_2(CO)_8$ and H_2 gases using on-line quadrupole mass spectrometry and Auger electron spectroscopy. Similar experiments using cobalt cyclopentadienyl dicarbonyl and H_2 reactants were also performed between 140 and 350 °C. For the dicobalt octacarbonyl precursor, film deposition rate and in-situ quadrupole mass spectroscopy results demonstrate that for all gas pulse times studied, film growth proceeds continuously at temperature as low as 60 °C, with no indication for self-limiting precursor adsorption. The observed continuous film growth with the $Co_2(CO)_8$ is related to the zero-valent metal center, where no reduction step is required to produce a reactive surface for adsorption. The cyclopentadienyl dicarbonyl precursor showed evidence for carbonyl cleavage and volatile Co(cyclopentadienyl), without film growth at less than 300 °C. In addition, the mass spectroscopy results show evidence for CH_4 and C_2H_6 production during Co film nucleation, with no hydrocarbons present during subsequent processing. This is consistent with an interesting self-catalytic effect of the cobalt nuclei that decreased upon continuous film formation.

5:00pm TF-MoA10 Reaction Mechanism Studies on ALD and CVD of Cobalt from Dicobalt Hexacarbonyl Tert-Butylacetylene, *T.Y. Park, K.W. Lee, J.S. Lee, D.O. Kim, J.S. Lee, H.T. Jeon, Y.D. Won*, Hanyang University, Korea Republic

Atomic layer deposition (ALD) and chemical vapor deposition (CVD) have been widely used to deposit many different materials in many different applications in the fields of semiconductors, and displays, recently. Generally, in these deposition methods they use MO precursors because of its high reactivity, liquid source and easy to control. In this study we tried to deposit Co film with MO precursor with two different deposition methods. There is very few precursors are available as a Co source and we chose CCTBA (dicobalt hexacarbonyl tert-butylacetylene) as Co source and hydrogen as a reactant gas. Reaction mechanism in both ALD and CVD was studied in the deposition system equipped with quadrupole mass spectrometer(QMS) and Auger electron spectroscope (AES). And we compared results with CVD and ALD. In this particular precursor CVD method give low impurity concentration and high growth rate compared to ALD grown films. This difference of impurity contents of cobalt films is due to their different reaction mechanism during deposition. In case of ALD, we think some of the ligands in a precursor were not broken completely and then incorporated into cobalt film during deposition. But for CVD, there was under 3% of carbon that was detected by AES (with RBS calibration). Therefore we will present the reaction mechanism of CCTBA precursor for depositing cobalt film by ALD & CVD method and the results that we analyzed this with in-situ QMS and AES.

5:20pm TF-MoA11 Excellent Si Surface Passivation Properties of ALD Al_2O_3 Films Studied by Optical Second-Harmonic Generation, *J.J.H. Gielis, B. Hoex, N.M. Terlinden, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Thin films of Al_2O_3 synthesized by (plasma-assisted) atomic layer deposition (ALD) provide an excellent level of surface passivation of c-Si and III-IV compound semiconductors, which is vital for the performance of devices such as nanocrystal or wafer-based light emitting diodes, photodetectors, and high-efficiency solar cells. Recently, it was demonstrated that the surface passivation properties of Al_2O_3 thin films arise after a postdeposition anneal.[1] In general, surface passivation can be achieved by a reduction of surface defects or by electrostatic shielding of charge carriers by internal electric fields (i.e., field-effect passivation). In this contribution the nonlinear optical technique of second-harmonic generation (SHG) has been applied to study Al_2O_3 thin films on c-Si substrates with interfacial SiO_x layers, both before and after anneal. SHG is

a surface and interface specific technique that is extremely sensitive to internal electric fields. Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 2.66-3.50 eV SHG photon energy range, has revealed the presence of negative fixed charge in the Al_2O_3. For as-deposited Al_2O_3 films the negative fixed charge density was found to be on the order of 10^{11} cm^{-2}, which increased to 10^{12}-10^{13} cm^{-2} after anneal. The corresponding internal electric field most likely accounts for the surface passivation properties of Al_2O_3 thin films after anneal. The important role of the negative fixed charge density in the passivation properties of Al_2O_3 was confirmed by carrier lifetime spectroscopy and capacitance-voltage measurements. In addition, real-time SHG experiments causing multiple-photon-induced charge trapping suggest a reduction of recombination channels after anneal, which could play an additional role in the surface passivation mechanism by Al_2O_3. It is straightforward to extend the approach discussed in this contribution to enable contactless characterization of charge and charging dynamics in c-Si/high-κ dielectric structures in situ and during processing, which provides not only relevant information on field-effect passivation but also for nonvolatile memory and CMOS transistor applications.

[1] B. Hoex et al. Appl. Phys. Lett. 89, 042112 (2006); Appl. Phys. Lett. 91, 112107 (2007).

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