

Tuesday Afternoon, November 1, 2011

Thin Film Division

Room: 107 - Session TF-TuA

ALD: Fundamental Reactions and Film Properties

Moderator: S.M. George, University of Colorado, Boulder

2:00pm **TF-TuA1 Indium Oxide Atomic Layer Deposition Facilitated by the Synergy between Oxygen and Water**, J.A. Libera, J.N. Hryn, J.W. Elam, Argonne National Laboratory

This study describes how In_2O_3 films can be prepared by ALD using alternating exposures to cyclopentadienyl indium (InCp) and combinations of H_2O and O_2 , even though H_2O and O_2 are ineffective when used individually. Nanostructured photovoltaics would benefit enormously from the capability to deposit conformal indium-tin oxide (ITO) films inside of high aspect ratio structures. For instance, our previous In_2O_3 ALD method using InCp and O_3 enabled ITO growth inside of anodic alumina membranes producing higher photocurrents through radial charge collection in dye-sensitized solar cells. However, this process yielded poor thickness conformality due to the In_2O_3 -catalyzed thermal decomposition of O_3 , and this shortcoming motivated our search for an O_3 -free process. We were surprised to discover that when H_2O and O_2 were used together, either as a simultaneous exposure (SE) or in the sequence H_2O - O_2 (WO) or O_2 - H_2O (OW), very uniform, highly conducting In_2O_3 films were deposited at 1.0-1.6 Å/cycle over large areas ($12'' \times 18''$) at temperatures as low as 100°C. *In-situ* quartz crystal microbalance, mass spectrometry, and Fourier transform infrared measurements revealed that the H_2O and O_2 work synergistically to facilitate the In_2O_3 ALD. Each molecule performs a necessary but distinct role in the growth mechanism. Next, we conducted a thorough study of this process for all three growth modes (SE, WO, OW) over the temperature range 100-250°C using spectroscopic ellipsometry, ultraviolet-visible transmission, X-ray diffraction, scanning electron microscopy, and Hall probe measurements. These measurements identified a remarkable correlation between the film structure and electrical properties around an amorphous-to-crystalline phase transition near the deposition temperature of 140°C.

2:20pm **TF-TuA2 Engineering AlN Thin Films by Atomic Layer Deposition on Wide Bandgap Semiconductors as Gate Dielectric**, Y.-C. Perng, J.P. Chang, University of California Los Angeles

Wide bandgap semiconductors, such as SiC and GaN, are known as base materials in electronic devices operating under high temperatures and high electric fields. Aluminum nitride (AlN) is a promising interfacial layer or dielectric material for SiC and GaN due to its material properties, such as wide bandgaps, similar atomic arrangement and small lattice mismatch (1.3% and 2.6%). Although various deposition methods, such as chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), have been used, synthesizing high quality AlN thin films for those applications is still an issue, especially in the view of controllability in atomic scales. Atomic layer deposition (ALD) is used to synthesize AlN thin layer on SiC, GaN and Si to achieve atomic controllability and assess the possibility to extend this deposition method to nitride growth and how the substrate properties affect the interface quality and corresponding electrical properties of the synthesized film

The AlN thin films were synthesized at 400~600°C via a chamber with the base pressure as 10^{-7} torr, using trimethylaluminum (TMA) and blue grade ammonia (NH_3) as precursors. The surface structure during the deposition was monitored via *in-situ* RHEED and the growth rate was 0.5~2 Å/cycle as a function of the deposition temperature. The surface composition, including the impurities, was found to be correlated to the deposition temperature, verified by *in-situ* x-ray photoelectron spectroscopy (XPS). The surface morphology of the films was studied by transmission electron microscopy (TEM) and atomic force microscope (AFM) and found to be conformal because the rms value was found to be less than 10 Å on SiC, which is the same as that of the substrate surface roughness. The capacitance/conductance-voltage characteristics were measured to determine the dielectric constant of the ALD film and interpret the interface states density, which were 8 and on the order of $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, respectively, comparable to that reported for MBE synthesized AlN.

2:40pm **TF-TuA3 Paul Holloway Award Lecture - Gas-Surface Interactions during Atomic Layer Deposition**, S. Agarwal*, Colorado School of Mines

INVITED

Atomic layer deposition (ALD) is an ideal technique for depositing amorphous and polycrystalline films that require atomic layer control over the film thickness and chemical composition, and can provide conformal coverage with sharp interfaces on high-aspect-ratio nanostructures. ALD has been used to deposit oxide, nitride, elemental and compound semiconductors, and metal films for various applications. The primary challenges in ALD are control over the film's microstructure and residual impurities, which in turn affect their structural, electrical, and transport properties. To overcome these problems, an understanding of atomic-scale events that occur during growth is required. In this presentation, we will discuss the mechanisms of the surface reactions of radicals and molecular precursors supplied during growth using a suite of *in situ* diagnostic tools. We will specifically discuss the reaction mechanisms during plasma- and ozone-assisted ALD of TiO_2 , Al_2O_3 , and SiO_2 , and how such reactions influence the film properties.

4:00pm **TF-TuA7 Mechanical Properties of ALD Thin Films**, H. Baumgart, Old Dominion University

INVITED

Atomic Layer Deposition (ALD) is recognized as the preferred method to deposit technologically important thin films of novel high-k dielectric metal oxides or semiconducting metal oxides for CMOS and MEMS technology with Angstrom accuracy. Large bodies of extensive studies exist on the electrical characterization of ALD films, however, there exists a lack of systematic studies regarding the mechanical properties of ALD grown thin films. Elevated temperatures cause phase changes in many ALD metal oxide films, which affect the mechanical properties and surface morphologies. Little is known about the impact of those phase changes on the nanomechanical properties of ALD HfO_2 . Phase change of ALD HfO_2 impacts the mechanical and electrical properties of high-k dielectric gate insulators depending on whether a Gate First or Gate Last process integration has been adopted. Nanoindentation is the most appropriate testing mechanism that accurately investigates the mechanical properties of extremely thin film specimens such as microcrystalline ALD thin films. Nanoindentation testing was conducted to investigate the impact of the different phase changes of HfO_2 on the mechanical properties. We have deposited ALD HfO_2 at low temperature and measured the mechanical properties of the various phase changes of HfO_2 following various thermal annealing cycles. After crystallization by annealing in a rapid thermal annealing (RTA) chamber, the modulus was found to decrease from $370 \pm 20 \text{ GPa}$ to $240 \pm 20 \text{ GPa}$ as the HfO_2 films transition from amorphous to polycrystalline structure past the phase change transition temperature of 600°C. Similarly, the hardness measurements reveal a high value of $18 \pm 1 \text{ GPa}$ for amorphous HfO_2 films and a decrease to $15 \pm 1 \text{ GPa}$ following the transition temperature to polycrystalline HfO_2 films.

Piezoelectric films such as ALD ZnO are finding applications in microelectromechanical systems (MEMS), piezoelectric transducers and oscillators, micro-resonators, gyroscopes, and energy harvesters. Since piezoelectricity of ZnO involves internal generation of electrical charge resulting from an applied mechanical force deforming the static structure of the ZnO crystals, studying the mechanical properties of novel ALD thin films of ZnO is important for these technical applications. Obtaining a better understanding of the structural and mechanical properties of novel ALD ZnO films is essential to improve key performance parameters of MEMS micro-devices.

An overview of the measured mechanical properties of selected ALD thin films will be presented. The mechanical properties of ALD thin films differ significantly from published values of bulk material.

4:40pm **TF-TuA9 Effect of Atomic Layer Deposition on the Mechanical Properties of Synthetic Nonwoven and Electrospun Polymer Fibers**, C.K. Devine, C.J. Oldham, J.S. Jur, G.N. Parsons, North Carolina State University

Nonwoven fiber mats and electrospun nanofiber films have been widely researched for their use in filtration, sensing, scaffolding for biological applications, and in many other areas. Nano- and microscale fibers can be functionalized using thin coatings deposited using ALD to impart mechanical strength, catalytic character, and increase conductivity while maintaining the fiber structure. We are interested in the mechanical properties of ALD coated micro and nano-sized fibers. Increasing the mechanical strength of these fibers allows for their use in more robust

* Paul Holloway Award Winner

applications; however it is desirable for the fibers to maintain their flexibility. For this study, nylon nanofibers formed by electrospinning were coated with either TiO₂ or ZnO at temperatures between 60 and 75°C, and the mechanical tear resistance was characterized by optical microscopy under the application of lateral strain. For the TiO₂ coated samples, the tear resistance remained the same when coated with smaller cycle numbers. As the films become thicker the mechanical properties are more dependent on the character of the coating. Specifically, after oxide coating, the fibers show a more brittle response to bending, resulting in visible cracking under optical microscopy after bending by less than 5° for thicker coatings. Similar trends are observed when nylon nanofibers are coated with ZnO or Al₂O₃, however, using our technique, the measureable change in mechanical response was observed at lower cycle numbers for ZnO and even lower for Al₂O₃, consistent with very different reactions between the nylon and the various ALD precursors. The difference in the tear resistance between these materials may be a result of the reactivity of the ALD precursors. Choosing a more robust and less brittle material to deposit on the fiber mats should improve their mechanical properties while maintaining the fiber structure and flexibility.

5:00pm **TF-TuA10 In Situ Studies of Oxide ALD for Crystalline Oxide Growth on Silicon**, *B.G. Willis, H. Wang*, University of Connecticut, *C. Zhang*, Chinese Academy of Sciences, China, *X. Jiang*, University of Connecticut

INVITED

Thin films of crystalline oxides integrated with silicon are of interest for novel electronic devices that utilize a rich variety of functional properties of oxide materials. These useful properties include piezoelectricity and ferroelectricity among others. Growth of crystalline oxides on silicon requires careful control of a nanometer thin transition region between the film and substrate to avoid deleterious side reactions such as oxidation of the substrate. Submonolayer surface reconstructions of alkaline earth metals such as Sr are critical for controlling the interface for successful growth. In this paper, we show how atomic layer deposition (ALD) can be used to precisely control the interface reactions for epitaxial growth. X-ray photoelectron spectroscopy and *in-situ* spectroscopic ellipsometry are used to monitor the growth and interface evolution of oxides deposited by ALD. Ellipsometry provides real time feedback on sequential adsorption cycles including precursor adsorption and oxidation. X-ray photoelectron spectroscopy provides detailed insight into the evolution of the interface structure during annealing and oxide desorption. Using this high degree of control enables the successful deposition of critical Sr/Si reconstructions for heteroepitaxy. The results show that ALD crystalline oxide heteroepitaxy is promising.

5:40pm **TF-TuA12 Nucleation and Interface Formation of Al₂O₃ on HF-treated InGaAs(100) by Atomic Layer Deposition**, *A.J. Muscat, B. Granados, F.L. Lie*, University of Arizona

III-V compound semiconductors are alternative channel materials for high-speed, low-power digital logic devices because their electron transport and breakdown properties are superior to that of Si. However, robust surface passivation processes and thermodynamically stable interfaces are barriers to its wider adoption. Additionally, the scaling down of integrated circuits has prompted the use of alternative high-*k* dielectric films to replace SiO₂ as the gate in metal-oxide-semiconductor field effect transistors (MOSFETs). Recent work demonstrated oxide removal and passivation of III-V surfaces by depositing high-*k* dielectrics using atomic layer deposition (ALD).

In this study, the ALD of Al₂O₃ was investigated on liquid and vapor HF-etched In_{0.53}Ga_{0.47}As(100) samples. Both half and complete ALD cycles of trimethylaluminum (TMA) and H₂O at 170°C were used to better understand nucleation and film growth. Aqueous HF etching was performed by a 49% HF dip 1 min and 15 s water rinse. *In situ* gas phase HF/H₂O etching was run at 29°C and 100 Torr with an HF to water partial pressure ratio of 1.23.

The initial 8.0±1.4 Å-thick native oxide contained 21% In, 27% Ga, and 52% As oxides and was reduced to a 4.3±1.5 Å-thick oxide containing 91±7% As by aqueous HF. In contrast, the gas phase HF produced ~7 Å-thick mixed oxide and fluoride overlayer containing 30% In, 40% Ga, and 30% As.

Large reductions of substrate oxides were observed after the first TMA pulse on both liquid and gas phase HF-treated samples. The intensity of the O 1s XPS peak was constant but the peak shifted by 1 eV to higher binding energy (BE) due to the conversion of the oxide to Al₂O₃. On the gas phase HF-treated samples removal of In, Ga and As atoms in the fluoride-rich overlayer layer was also observed after the first TMA pulse. The intensity

of the F 1s peak was reduced and the peak shifted by 2.2 eV to higher BE, indicating the etching of fluoride as well as the conversion of the bonding from substrate fluorides to Al-F.

Subsequent H₂O and TMA pulses up to three cycles of TMA/H₂O revealed a systematic peak shift of the overlayer atom signals. F 1s, O 1s and Al 2p peaks shifted 0.9 eV, 0.4 eV and 0.2 eV, respectively, towards lower BE after a H₂O pulse and shifted back to their original positions after a TMA pulse. The systematic shifts could be attributed to the change in surface termination after every half-cycle reaction, methyl termination after the TMA pulse and hydroxyl termination after a water pulse. Understanding surface reactions involved in the nucleation phase and early cycles of ALD is important in achieving control of the III-V-dielectric interface.

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