Thin Film
Room: 114 - Session TF+SS-WeM

ALD Surface Reactions and Precursors
Moderator: Sean Jones, National Science Foundation (NSF), Paul Poodt, Solliance/TNO

8:00am **TF+SS-WeM1 High Performance Precursors for Atomic Layer Deposition of Silicon Containing Films**, ***Anu Mallikarjunan***, Air Products and Chemicals, Inc. **INVITED**

Conformal and continuous silicon containing films produced by Atomic Layer Deposition (ALD) are enabling novel processing schemes and integrated device structures. The increasing drive towards lower temperature processing requires new precursors with even higher reactivity. A systematic method for identification of high performance precursors is thus very desirable, and needs to incorporate fundamental understanding of precursor chemistry, surface reactions; and relationships between precursor structure and deposited films. The overall approach accordingly relies on integrating molecular and surface reaction modeling, the ability to synthesize stable precursors with reactive groups, in-situ surface studies, and thin film deposition testing. To illustrate this approach, two case-studies will be discussed in this presentation: silicon oxide and silicon nitride ALD. In both cases, a representative monoaminosilane ($R^1R^2N)SiH_3$ called di - sec- butylaminosilane (DSBAS) will be studied. The impact of changing the precursor structure will also be discussed.

8:40am **TF+SS-WeM3 Amorphous In_2O_3 and Sn-doped In_2O_3 Layers by ALD Prepared using Trimethyl Indium and Ozone**, ***Anil Mane***, *A. Allen,* Argonne National Laboratory, *R. Kanjolia,* SAFC Hitech, *J. Elam*, Argonne National Laboratory

Abstract:

Among the transparent conducting oxides (TCOs), Indium oxide (In_2O_3) possesses a wide band gap of 2.9 Ev at room temperature yielding high optical transparency and also exhibits good chemical stability. When doped with tin to form Indium tin oxide (ITO), the electrical conductivity increases greatly allowing this material to be used in a wide range of applications including touch screens displays, light-emitting diodes, liquid crystal displays, and sensors. Further amorphous TCOs have several advantages over their crystalline microstructures e.g. lower temperatures deposition which tend to simplify the deposition methods for mainly for plastics for flexible electronics. The lack of grain boundaries in amorphous materials, isotropic nature allows a simpler scheme for uniform etching with lower surface roughness. Unlike crystalline TCOs, the amorphous TCOs electrical and optical are also strongly influenced by the oxygen content of the films. As ALD offers the potential to deposit ITO over large areas at low temperature with high uniformity to address some of these applications, but the viability of this method hinges on developing a robust In_2O_3 ALD process. Trimethyl indium (TMIn) is an attractive economical precursor for In_2O_3 ALD because it offers the advantages of a high vapor pressure and availability in high volume.

In this study we examined the ALD of In_2O_3 using alternating exposures to TMIn and different oxygen sources: O_3 (ozone), O_2, H_2O, and H_2O_2. We first used in situ quartz crystal microbalance (QCM) and mass spectrometry measurements to evaluate the effectiveness of the different oxygen sources and found that only ozone yielded sustained growth. These measurements also provided details about the In_2O_3 growth mechanism and enabled us to verify that both the TMIn and the O_3 surface reactions were self-limiting. Next, we prepared ALD In_2O_3 films on a variety of substrates and characterized them using X-ray diffraction, UV-vis. Spectrometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy, Hall probe measurements, scanning electron microscopy, and atomic force microscopy. We found that at deposition temperatures of 100-200ºC the amorphous growth per cycle was nearly constant at ~0.4 Å/cycle and the films were dense and pure. At higher growth temperatures the In_2O_3 growth rate increased due to thermal decomposition of the TMIn. We succeeded in doping the amorphous In_2O_3 films with tin by substituting tetrakis-(dimethylamino) tin for the TMIn in a fraction of the growth cycles and observed that the electrical conductivity improved substantially in these films.

9:00am **TF+SS-WeM4 Towards Organic Electronics: Atomic Layer Like Deposition of ZnS and ZnO on Organic Thin Films**, *Z. Shi,* ***Amy Walker***, University of Texas at Dallas

We discuss our recent studies of atomic layer like deposition (ALLD) of ZnS and ZnO on organic thin films using diethyl zinc (DEZ) as the zinc source. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. We show that a detailed understanding of the reaction pathways is critical for controlling the properties of ZnO and ZnS films grown by ALD. For both ZnO and ZnS ALLD, the growth rates on –COOH terminated SAMs are approximately 10 % lower than on –OH terminated SAMs. As expected on −OH terminated SAMs, the DEZ reacts with the hydroxyl group. However, on –COOH terminated SAMs DEZ reacts with both the carbonyl and hydroxyl bonds present leading to the formation of a ketone rather than deposition. Further, the composition of the deposited layer and its growth can be affected by the functionality of the surface. For ZnO ALLD, on-COOH terminated SAMs XPS indicates that the initial composition of the layer is similar to $Zn(OH)_2$. In contrast on –OH terminated SAMs the deposited layer is always composed on ZnO. The growth of the layer also appears to be different. On –COOH terminated SAMs, the layer growth is more two dimensional (layer-by-layer) while on –OH terminated SAMs, the growth appears to proceed via the formation of islands.

9:20am **TF+SS-WeM5 AlF_3 Atomic Layer Deposition or Al_2O_3 Atomic Layer Etching from Sequential Exposures of Trimethylaluminum and HF**, ***Jaime DuMont***, *Y. Lee, S.M. George*, University of Colorado at Boulder

Sequential exposures of $Al(CH_3)_3$ [trimethylaluminum (TMA)] and HF can lead to either AlF_3 atomic layer deposition (ALD) or Al_2O_3 atomic layer etching (ALE). The observation of AlF_3 ALD or Al_2O_3 ALE depends on temperature and pressure. AlF_3 ALD occurs at lower temperatures and higher pressures. Al_2O_3 ALE of an initial Al_2O_3 film occurs at higher temperatures and lower pressures. The AlF_3 ALD or Al_2O_3 ALE were investigated using *in situ* Fourier transform infrared (FTIR) spectroscopy and quartz crystal microbalance (QCM) measurements.

The FTIR analysis observed AlF_3 ALD or Al_2O_3 ALE by measuring the absorbance gain of Al-F stretching vibrations in AlF_3 or the absorbance loss of Al-O stretching vibrations in Al_2O_3. At lower temperatures, the HF exposures react with the underlying Al_2O_3 surface to form AlF_3 and HF molecules on the surface. TMA molecules subsequently react with HF on the surface to yield $AlF(CH_3)_2$ surface species. $AlF(CH_3)_2$ is then converted to AlF_3 with the next HF exposure producing AlF_3 ALD. At higher temperatures, the HF exposures react with the underlying Al_2O_3 surface to form AlF_3 and fewer HF molecules absorb on the surface. TMA then accepts fluorine from AlF_3 to form $AlF(CH_3)_2$ which desorbs from the surface and leads to etching of the initial Al_2O_3 film.

The effect of pressure was also explored by adjusting the N_2 carrier gas flow from 0-150 sccm to vary the background pressure from 30 mTorr to 1.6 Torr. These FTIR experiments revealed that the transition from AlF_3 ALD to Al_2O_3 ALE occurred at higher temperatures for higher background pressures. The higher pressures apparently produce a "cage effect" and increase the lifetime of the $AlF(CH_3)_2$ surface species that leads to AlF_3 ALD. The QCM experiments measured an AlF_3 ALD growth rate that progressively decreased at higher temperatures and went negative at >250°C when TMA and HF etched the AlF_3 or Al_2O_3 films.

9:40am **TF+SS-WeM6 A Comparison of Water Delivery Methods for Atomic Layer Deposition**, ***Tariq Ahmido***, *W.A. Kimes, B.A. Sperling, J.E. Maslar*, NIST

Water is frequently used as an oxygen source for atomic layer deposition (ALD) of metal oxides. However, water exhibits a relatively high vapor pressure at room temperature and readily adsorbs on reactor surfaces. These characteristics can make it difficult to reproducibly control water delivery during ALD, particularly when small quantities are desired. The focus of this work is characterizing and comparing three different methods of water vapor delivery in an effort to identify techniques for ensuring reproducible delivery of water vapor quantities. For this investigation, three methods of water injection were compared. The first method utilizes a needle valve between the water reservoir and the water injection valve (the valve that controls the water allowed into the delivery line to the reactor). This method is commonly employed for research grade reactors as the use of an adjustable orifice permits the water flow rate to be varied. However, control of small water quantities can be difficult due to the buildup of water vapor between the needle valve and the water injection valve. The second method overcomes this control limitation by utilizing a pump to vent water vapor from the volume between the needle valve and injection valve prior to

injection into the delivery line. This method provides a high degree of control at the cost of added complexity and expense. The third method utilizes a laser-drilled orifice in a VCR gasket as the flow-controlling orifice. This method is simple and inexpensive, however, water flow rates cannot be adjusted without changing the orifice. The performance of these three water injection methods was characterized using an optical water mass flow meter (MFM) that has been developed to rapidly quantify water vapor. This MFM was based upon a wavelength modulation spectroscopic technique utilizing a near-infrared diode laser. This MFM permits quantitative comparison of the performance of these three water injection methods, allowing a potential user to identify method suited to a particular application.

11:00am **TF+SS-WeM10 Stoichiometric Dependence of the Interface of HfO_2 ZrO_2, TiO_2, Ta_2O_5 and La_2O_3 on Si (100) by ALD**, ***Pierre Mani***, Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *E. Lopez,* Universidad Autónoma de San Luis Potosí, Mexico, *H. Leos,* Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *H. Hernandez,* Universidad Autónoma de San Luis Potosí, Mexico, *J.A. Hernandez, J.R. Farias, J.T. Elizalde,* Universidad Autónoma de Ciudad Juárez-IIT, Mexico, *M.A. Melendez,* CINVESTAV, Mexico, *M.A. Vidal*, Universidad Autónoma de San Luis Potosí, Mexico

A systematic analysis was performed to determine the characteristic times of surface coverage of oxidant-agent on silicon substrates (100) by the atomic layer deposition (ALD) method in order to ensure the saturation of the surface substrate for growth. The aperture-times of the precursors have been studied due to stoichiometric impact of the layers and also at the interface. The numbers of cycles were critical for the interface formation at the early stage growth. This work emphasizes in the study and analysis between interface of high k dielectric layer and amount of cycles as function of layers and stoichiometric interface. Previous works complement with results obtained in study the growth of hafnium oxide and titanium oxide by atomic layer deposition (ALD) demonstrating the close relationship between the thickness and composition of the interface layer with the number of cycles performed by the ALD and with the aperture-time of the precursors. This analysis shows a base that will allow create HfO2 ZrO2, TiO2, Ta2O5, La2O3 nanofilms with optimal characteristics.

11:20am **TF+SS-WeM11 In-situ Infrared Study of Atomic Layer Deposition of Molybdenum Nitride using Bis(tert-Butylimido)-Bis(dimethylamido) Molybdenum and Hydrazine**, ***Abraham Vega***, *C.E. Nanayakkara,* The University of Texas at Dallas, *G. Liu, R. Kanjolia,* SAFC Hitech, *Y.J. Chabal*, The University of Texas at Dallas

Molybdenum nitride films have properties such as high hardness, high melting point, good chemical stability and high conductivity, which makes them suitable for a wide range of technological areas, as diffusion barriers or interconnections in microelectronics and even as catalysts in fuel cells. Molybdenum nitride films have been deposited by variety of techniques, such as chemical vapor deposition, magnetron sputtering, and atomic layer deposition among others.

For atomic layer deposition of molybdenum nitride, molybdenum complexes containing alkylamido and alkylimido ligands are being considered as potential molybdenum precursors. A notable advantage is that they do not produce corrosive byproducts compared to halide based transition metal precursors.[1] A uniform growth has been achieved in the range 260 – 300 ^{0}C with bis(tert-butylimido)-bis(dimethylamido)molybdenum when used with NH_3 as a co-reactant.[1]

In this study, *in-situ* IR and X-ray photoelectron spectroscopies are used to investigate ALD of bis(tert-butylimido)-bis(dimethylamido)molybdenum and hydrazine an alternative for NH_3 as co-reactant for molybdenum nitride deposition on pre-annealed, oxidized and OH-terminated Si(100) surfaces. While bis(tert-butylimido)-bis(dimethylamido) molybdenum is expected to react with two surface OH groups leaving one amino groups with further reaction with hydrazine leading to a NH_x-terminated surface, the details of the reactions have not been explored, hence the importance of *in-situ* IR spectroscopy.

Bis(tert-butylimido)-bis(dimethylamido) molybdenum reacts with surface Si-OH groups (loss at 3740 cm^{-1}) to form the expected $(O)_2$-Mo=(N-tBu)$_2$structure, as evidenced by broad band from various CH_x stretch bands in the 2900 cm^{-1} region and stretching of CN bonds at 1240 cm^{-1}, respectively. The first hydrazine pulse leads to a loss of tBu vibrational bands [at 2900 and 1240 cm^{-1}]. The steady state ALD process is characterized by tBu removal by hydrazine and formation of NH_x groups driving the ALD process. A clear ligand exchange is observed at deposition temperatures of 225, 250 and 275 $^{\circ}$C for 30 cycles. The ALD window for this process was found to be between 225 and 275 $^{\circ}$C, with low carbon content determined by XPS, which is lower than the window when using NH_3 (260-300 °C) instead of hydrazine. No growth is observed above 300 °C, and very poor quality films are obtained at 200°C.

This work confirms the reactivity of bis(tert-butylimido)-bis(dimethylamido) molybdenum with OH-terminated surfaces at low temperatures and illustrates the role of the co-reactant on the thermal window and the quality of the resulting molybdenum nitride films.

1. Chem. Mater., Vol. 19, No. 2, 2007

11:40am **TF+SS-WeM12 Atomic-Layer-Deposited In_2O_3:H Transparent Conductive Oxides: How to Achieve the Best Possible Carrier Mobility**, ***Bart Macco****, Eindhoven University of Technology, Netherlands, *H.C.M. Knoops,* Oxford Instruments Plasma Technology, UK, *M.A. Verheijen, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, we have reported on an atomic layer deposition (ALD) process to prepare H-doped indium oxide (In_2O_3:H) transparent conductive oxides (TCOs) with an extremely high carrier mobility (138 cm^2/Vs) and low resistivity (0.27 mΩcm) at low processing temperatures (<200 ºC) [1]. This high carrier mobility is especially promising for silicon heterojunction solar cell applications, as it allows for a low resistivity at low carrier density, thereby nullifying parasitic free carrier absorption in the infrared. Here we focus on new insights into the physical mechanisms during the preparation process and explain how such high mobility can be obtained through analysis of the electron scattering and doping mechanisms.

The preparation starts with ALD of In_2O_3:H at 100 ºC using InCp, H_2O and O_2 as growth precursors. The films are amorphous, although a low density of very small crystallites is present. Subsequently the films are crystallized by annealing at 150-200 ºC. Electron microscopy reveals that crystallization proceeds from grain growth from the pre-existing crystallites without additional nucleation, which makes the final grain size and optoelectronic properties independent of annealing temperature. The resulting crystals extend over the film thickness of 75 nm and have a typical lateral size of a few hundred nm. Analysis of the grain growth by electron microscopy shows a thermally activated behavior, with an activation energy of 1.4 eV.

A combination of temperature-dependent Hall measurements and spectroscopic ellipsometry has been employed to distinguish between the various scattering mechanisms and dopants in crystallized In_2O_3:H films. Key results include the fact that carrier mobility is only limited by ionized impurity and phonon scattering processes and that other extrinsic defect scattering such as neutral impurity and grain boundary scattering can be neglected. Since only unavoidable scattering processes play a role, this means that this TCO has the highest possible mobility at this carrier density. The analysis also excludes a significant contribution from doubly charged donors (i.e. oxygen vacancies), and the source of doping is confirmed to be singly charged H. Furthermore, by comparison of the absolute H-concentration and the carrier density in crystallized films, it is deduced that <4 % of the incorporated H is an active dopant in crystallized films. Therefore, it can be concluded that inactive H atoms do not contribute to defect scattering, which explains why In_2O_3:H films are capable of achieving a much higher carrier mobility than conventional In_2O_3:Sn films.

[1] Macco et al., *P.S.S. - Rapid Res. Lett.*, DOI: 10.1002/pssr.201409426

12:00pm **TF+SS-WeM13 Mechanical Property and Corrosion Resistance Evaluation of CrVN and CrSiN Thin Films Grown by a Hybrid High Power Impulse Magnetron Sputtering and Radio Frequency Sputtering Technique**, ***Jyh-Wei Lee***, *C.Y. Cheng, P.W. Chang,* Ming Chi University of Technology, Taiwan, Taiwan, Republic of China, *B.S. Lou*, Chang Gung University, Taiwan, Taiwan, Republic of China

High power impulse magnetron sputtering (HIPIMS) is a novel coating technology, which is characterized for its high peak power density to achieve unique thin film properties, such as high hardness, good adhesion and tribological performance. The aim of this work was to systematically study the microstructure, mechanical properties and corrosion resistance of CrVN and CrSiN coatings fabricated by a hybrid high power impulse magnetron sputtering and radio frequency sputtering technique. The experimental results showed that the peak power density increased linearly as the duty cycle decreasing from 5% to 2.5%. As compared with the CrVN coating, the higher hardness and better corrosion resistance were obtained for the CrSiN coatings, which can be attributed to their denser microstructures fabricated using the HIPIMS technology under optimal duty cycle and pulse frequency in this work. Effects of Vanadium and Silicon elements on the microstructure, mechanical and electrochemical properties of CrVN and CrSiN coatings were also discussed.

*** TFD James Harper Award Finalist**

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