Thin Film
Room: B4 - Session TF2-TuA

ALD/CVD: Oxides and Barriers
Moderator: S.M. Rossnagel, IBM Research

2:20pm **TF2-TuA2 Evaluation of Al_2O_3 ALD Gas Diffusion Barriers and Visualization of Barrier Defects Using the Ca Test**, ***J.A. Bertrand***, *S.H. Jen, D. Seghete, S.M. George*, University of Colorado, Boulder

Flexible gas diffusion barriers are required on polymers. One key application area for these barrier films is organic electronics, especially organic light emitting diodes (OLED) for flexible displays.The necessary water vapor transmission rate (WVTR) for OLEDs is $<10^{-6}$ g/m^2/day. In collaboration with DuPont, we earlier measured low WVTR values of ~6.5 x 10^{-5} g/m^2/day for single Al_2O_3 ALD films at 60°C/85% RH using the Ca test with optical transmission probing (*Appl. Phys. Lett.*89, 031915 (2006)). Our current measurements have employed the Ca test with electrical resistance probing. The electrical resistance probing method is based on previous work by Paetzold and coworkers (*Rev. Sci. Instrum*. 74, 5147 (2003)). The change of the electrical resistance of the Ca film versus time can be related to the WVTR.

The current results are also obtained using a new ALD reactor that is connected to a glove box that is interfaced to a PVD chamber. This apparatus allows Ca test films to be prepared, transferred into the glove box and then positioned in the ALD reactor all under oxygen-free conditions. The glove box also helps to reduce particle contamination that may be the dominant factor in determining the WVTR. Using this apparatus, we have measured even lower WVTR values of ~2 x10^{-5} g/m^2/day at 70oC/28% RH with an Al_2O_3 ALD film thickness of 25 nm. This is the lowest WVTR value measured at elevated temperature for a single layer barrier film.

The Al_2O_3 ALD barriers are also deposited directly on the Ca films. This configuration allows the Ca test film to visualize the defects in the Al_2O_3 ALD barrier. As the calcium oxidizes, the transition from shiny metal to clear calcium oxide can monitor the number and distribution of defects in the Al_2O_3 ALD film. The experiments demonstrate that the calcium oxidation is dominated by a few pinhole defects. The WVTR value of ~2 x 10^{-5} g/m^2/day is consistent with several defects per cm^2 in the Al_2O_3 ALD film. The resistance increases as these pinholes lead to the oxidation of circular regions of the Ca film that grow with time.

2:40pm **TF2-TuA3 Atomic Layer Deposition of TiO_2 on Si (100) and GaAs (100) Surfaces**, ***T. Gougousi***, *J.W. Lacis,* UMBC, *J.D. Demaree*, ARL

Atomic Layer Deposition (ALD) has been used to deposit TiO2 films on Si (100) and GaAs (100) surfaces from tetrakis dimethylamino titanium (TDMATi) and H2O at 200°C. The growth rate is measured at ~.6Å/cycle by High Resolution Transmission Electron Microscopy (HRTEM) and spectroscopic ellipsometry, and Rutherford Backscattering measurements indicate steady state Ti atom coverage of ~1.4x1015 cm-2. As deposited films are slightly overoxidized (O/Ti~2.2) and are amorphous, but inert anneals above 500°C result in film crystallization mainly in the rutile phase. When films are deposited on native oxide GaAs surfaces an interface cleaning reaction is observed. The starting surface consists of ~26Å of gallium and arsenic native oxides. X-ray photoelectron spectroscopy indicates that the surface oxides are consumed gradually during the ALD process and that after 120 and 250 process cycles only about a monolayer of metallic arsenic-arsenic suboxide and gallium suboxide persists at the interface and the conclusions are corroborated by HRTEM data. The results for the TiO2/GaAs interface will be compared to that obtained for the HfO2/GaAs interface using two different but similar ALD chemistries that utilize amide precursors (TEMAHf and TDMAHf). All three ALD chemistries indicate the presence of an "interface cleaning" mechanism similar to what has been observed for other amide-precursor-based ALD processes. [1] [2] [3]

[1] 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)

[2] C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, H. C. Kim, J. Kim, and R. M. Wallace, Appl. Phys. Lett. **92**, 071901 (2008)

[3] J.C. Hackley, J.D. Demaree, and T. Gougousi, Appl. Phys. Lett. **92**(16), 162902 (2008).

3:00pm **TF2-TuA4 Self-limiting Deposition of Anatase TiO_2 for Photocatalytic Applications**, ***N.G. Kubala***, *C.A. Wolden*, Colorado School of Mines

Titanium dioxide thin films were deposited using pulsed plasma-enhanced chemical vapor deposition at low temperature (T_s <200 ºC). Self-limiting deposition (~1 Å/cycle) was accomplished via simultaneous delivery of $TiCl_4$ and O_2. $TiCl_4$ is shown to be inert with molecular oxygen at process conditions, making it a suitable precursor for pulsed PECVD. The process was examined as a function of $TiCl_4$ exposure, plasma power, and substrate temperature. Crystalline anatase formation was observed at temperatures as low as 120°C. Depositions at high power also had a significantly greater refractive index. For process conditions, digital control over film thickness is demonstrated. Film uniformity is exceptional, with thickness variations less than 1% across 100 mm silicon wafers. Photocatalytic activity has been examined using methylene blue decomposition experiments, UV-VIS spectroscopy, and electrochemical analysis. Mott-Schottky plots show that the band edge position of these thin films is in agreement with measurements from anatase single crystals. The photocatalytic activity of these films for both hydrogen production and organic remediation is assessed. We also plan to present new results on the production of the titania-vanadia alloys with enhanced light response in the visible regime.

4:00pm **TF2-TuA7 *In situ* X-ray Photoelectron Spectroscopy for the Study of Initial Stages of TiO_2 ALD on Silicon**, ***R. Methaapanon***, Stanford University

Titanium dioxide (TiO_2) is one of the widely studied atomic layer deposition (ALD) systems due to its outstanding electrical and optical properties that are suitable for variety of applications. The properties of the deposited TiO_2, especially at the interface with the substrate, become more important as the size of required devices in each application approaches the nano-scale. Due to different chemical properties of the substrate and the deposited material, nucleation at the interface can be different from the steady state growth of the bulk.

In this work, TiO_2 ALD is carried out in an integrated ALD reactor/UHV chamber that allows for X-ray photoelectron spectroscopy (XPS) analysis after each precursor pulse without vacuum break. Titanium tetrachloride ($TiCl_4$) and water (H_2O) are selected as precursors due to their molecular simplicity and broad operating temperature range that result in several achievable TiO_2 phases. The initial growth at 100°C on two substrates − chemical oxide on silicon prepared by piranha treatment, and hydrogen-terminated silicon prepared by HF etch − is compared. The intensities and binding energies of characteristic peaks from the XPS spectra are used to analyze the elemental compositions and chemical state of each species as the deposition progresses. TiO_2 growth on both SiO_2 and H-Si surfaces exhibits linear behavior, as normally achieved by ALD, but the TiO_2 growth rate is lower on hydrogen-terminated surface than on silicon dioxide surface. Interestingly, no incubation period is observed on either surface.

The chemical shifts of the Si 2p, O 1s and Ti 2p XPS peaks after TiO_2 deposition on the SiO_2 substrate suggest bond formation between titanium and silicon-bound oxygen at the interface. The data also suggest that some chlorine is trapped at the SiO_2/TiO_2 interface and that the titanium oxide right at the interface is sub-stoichiometric. The results on the hydrogen-terminated Si surface show different interfacial properties. There is no detectable amount of oxidized silicon species on hydrogen-terminated silicon after deposition under vacuum. Together with the results of *ex situ* studies, it can be concluded that interfacial silicon dioxide grows after air exposure, not during ALD reactions. The absence of silicon oxide and a shift in the Si 2p binding energy in the as-grown samples suggest the possibility of an ALD mechanism which involves direct bonding between titanium and silicon on the surface. The differences between the two substrates will be discussed.

4:20pm **TF2-TuA8 Plasma-Assisted Atomic Layer Deposition of Titanium Dioxide: Reaction Mechanism Studies using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy**, *V. Rai,* ***S. Agarwal***, Colorado School of Mines

In this presentation, the authors will discuss the surface reaction mechanism during the plasma-assisted atomic layer deposition (ALD) of TiO_2 using titanium tetraisopropoxide and an O_2-Ar plasma at substrate temperatures ≤150 °C. In situ attenuated total reflection Fourier-transform infrared (IR) spectroscopy was used to detect surface species generated or consumed during each half-reaction cycle with a sensitivity down to a fraction of a monolayer. Our IR data showed that the reactive species on the TiO_2 surface for TTIP chemisorption were *both* surface carbonates and –OH groups, identified in the 1450-1700 and 3400-3800 cm^{-1} regions, respectively. Based on this observation, we conclude that plasma-assisted

ALD of TiO_2 involves a combination of the mechanisms previously reported for O_3- and H_2O-based ALD using TTIP as the metal precursor: we had recently reported surface carbonates as the reactive sites using O_3 as the oxidizing agent and –OH groups have previously been reported with H_2O as the oxidant. We hypothesize the following reaction mechanism. Combustion products such as CO_2, CO, and H_2O are formed during the O_2-plasma cycle due to the plasma-assisted combustion of the isopropoxy ligands on the surface. A fraction of this CO_2 reacts with the surface to generate the carbonates, similar to the O_3-based ALD mechanism. We explain the simultaneous presence of the surface –OH groups in addition to the carbonates due to the plasma activation of H_2O, also generated during the O_2 plasma cycle, and the subsequent reaction of these activated species with the surface. The latter step does not occur when O_3 is used as the oxidant. In fact, the ratio of the carbonates and the surface –OH groups could be varied by controlling the residence time of the reaction products in the plasma. A growth per cycle of ~0.8 Å was obtained at 150 °C, which was significantly higher compared to H_2O- and O_3-based ALD of TiO_2 at similar temperatures. In situ and ex situ IR measurements showed no significant carbon contamination in the films. Ex situ IR data showed the Ti-O-Ti transverse optic mode at 440 cm^{-1}, a characteristic of anatase. The ex situ x-ray diffraction measurements further confirmed anatase as the dominant crystal phase. The crystallinity of the films may be the reason for the higher growth per cycle compared to that observed for amorphous films deposited from the same metal precursor.

4:40pm **TF2-TuA9 Molecular Layer Deposition of "Sugarcone" Hybrid Organic-Inorganic Films Using Saccharides and Metal Precursors**, ***B. Yoon***, *R. Hall, D. Seghete, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Molecular layer deposition (MLD) of hybrid organic-inorganic polymers is based on the sequential, self-limiting reactions of organic and inorganic reactants. Alucone MLD has been reported based on the reaction between trimethylaluminum (TMA) and ethylene glycol (EG). Zincone MLD has also been demonstrated using diethylzinc and EG as the reactants. In this study, a new class of hybrid organic-inorganic films that can be called "sugarcone" was fabricated based on the reaction between saccharides and metal reactants. This strategy was demonstrated using sucrose and TMA. The sugarcone MLD film growth was monitored using in situ transmission FTIR analysis. The FTIR spectra revealed that TMA reacts with hydroxyl groups and deposits $AlCH_3$* species. The sucrose then reacts with the $AlCH_3$* species and deposits an organic moiety with available hydroxyl groups. Both the TMA and sucrose sequential reactions were self-limiting. Sequential exposures of TMA and sucrose led to the linear growth of the sugarcone film. X-ray reflectivity measurements were consistent with a growth rate of ~ 2.0 Å per cycle based on 300 MLD cycles on a Si wafer at 150°C. The TEM images of sugarcone films on ZrO_2 nanoparticles after 150 MLD cycles at 150°C were in agreement with a MLD growth rate of ~2.3 Å per cycle. The sugarcone films were not stable in air and oxidized by adsorbing H_2O. This reaction may be useful in gas diffusion barriers because the sugarcone film could serve as a chemical getter to adsorb any H_2O that diffuses through the barrier.

5:00pm **TF2-TuA10 *In-situ* Half-Cycle XPS Investigation of La-aluminate Formation during Atomic Layer Deposition**, ***T.J. Park***, *H.C. Kim, M. Milojevic, B. Lee, R.M. Wallace, J. Kim,* University of Texas at Dallas, *X. Liu, M. Rousseau, J.H. Li, H. Li, D. Shenai, J. Suydam*, Dow Electronic Materials

Lanthanum based oxide (La_2O_3) having outstanding high dielectric constant of 30 has been extensively investigated because it can provide a generous thickness margin as well as a considerable leakage current reduction which is essentially required in modern device applications. However, the hygroscopic and catalytic nature of La ions lead s to formation of either La-hydroxide ($La(OH)_3$) or La-silicate ($LaSiO_x$) resulting in degradation of device properties. The formation of La-hydroxide can cause serious issues such as shifting of flat band voltage (V_{fb}), increased gate leakage and increased the surface roughness. La-hydroxide may also cause a CVD reaction, ruining the self-limited nature of ALD reaction during conventional water based ALD process. Also, direct deposition of La_2O_3 on Si substrate has a significant amount of La-silicate phase in the grown film by the interfacial reactions with the Si. In order to overcome these intrinsic problems of pure La-oxide, some of researches have been carried out using an addition of aluminum oxide (Al_2O_3) layer in the pure La_2O_3 film. La-aluminate is potentially stable on Si substrate having less opportunity to form an interfacial layer. In addition, La-aluminate has enhanced stability to water ambient due to a gettering effect of Al_2O_3. In this presentation, we will focus on the detailed growth mechanisms of La-aluminate during a water based ALD process. In order to investigate initial interfacial reactions during ALD, we investigate *in-situ* half cycle reactions by means of x-ray photoelectron spectroscopy analysis following individual ALD pulses of tris(N,N'-diisopropylformamidinato) lanthanum [La(^{i}PrfAMD)$_3$], trimethyl-Al (TMA) and water (H_2O) at a deposition temperature of 300°C. The La-aluminate sample was transferred from an ALD reactor after every individual pulse of La, Al and H_2O to a monochromatic x-ray photoelectron spectroscopy (XPS) chamber via ultra high vacuum (UHV) chamber maintaining a vacuum level of less than 10^{-11} torr. This experimental technique enables us to investigate evolution of chemical binding status without exposure to air as the number of ALD half cycle increases. Additionally, residual C and N in the films will be also discussed.

5:20pm **TF2-TuA11 Engineering Optical Properties by Controlling Concentration and Proximity of Rare Earth Dopants in an Y_2O_3 Host using Radical Enhanced ALD**, ***J. Hoang***, *J. Chang*, University of California, Los Angeles

The realization of compact fiber optic networks is limited by the control of the rare earth (RE) dopant ion's identity and its distribution. Each RE ion contains spectral energy levels, whose transitions can be promoted by controlling the ion-ion proximity. In this work, a radical enhanced atomic layer deposition (RE-ALD) process, utilizing highly reactive radicals to activate surface reactions, is developed to design complex metal oxides with multiple dopants, whose concentration variation and spatial distribution control enable the synthesis of a wide range of multifunctional materials with tunable properties including magnetic, spectral, and electronic. Specifically, the control of dopant proximity and concentration is used to enhance desirable spectral transitions related to amplification at 1.54 micron for compact planar optical amplifier applications. The spatial distributions between Er^{3+} and various rare earth sensitizers (e.g. Yb and Eu) are investigated. The ability to control the spacing of each sensitizer allows for a unique study of the correlation between energy transfer and dopant proximity. Thin films of approximately 10 nm are synthesized by sequential radical-enhanced ALD of Y_2O_3, Er_2O_3, Yb_2O_3, and Eu_2O_3 at about 350°C. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films were determined by x-ray photoelectron spectroscopy, electron microscopy and photoluminescence measurements. To optimize the effect of the sensitizer and minimize the concentration quenching, the concentration and spatial distance between Yb^{3+}/Eu^{3+} sensitizers and Er^{3+} were controlled by changing the global deposition cycle sequence. Extended x-ray absorption fine structure analysis verified the spatial control of dopants in the Y_2O_3 host. It was found that multi-dopant spatial control allows for incorporation of minimal active sensitization sites, allowing for the possibility of maximizing the active Er concentration while maintaining efficient energy transfer. This additional degree of control allows for a class of complex materials that can potentially outperform their conventional counterparts by many-folds in luminescence.

5:40pm **TF2-TuA12 ALD of La Stabilized Amorphous HfO_2 High-k Dielectric Thin Films**, ***T. Wang***, *J.G. Ekerdt*, University of Texas at Austin

La_2O_3 was incorporated into hafnium dioxide grown by atomic layer deposition (ALD) to stabilize the amorphous phase during high temperature annealing. The incorporation was achieved by depositing HfO_2 and La_2O_3 alternatively in different ALD cycles. X-ray photoelectron spectroscopy compositional analysis shows that the Hf and La atomic percentage ratio can be controlled by varying the number of separate Hf and La ALD cycles. Microstructure was determined with X-ray diffraction and cross-sectional transmission electron microscopy. The introduction of La increases the film crystallization temperature from 5 00 °C for a HfO_2 film to 800 °C, 900 °C and 950 °C for 10 nm films containing 13% La (metal basis), 25% La and 43% La, respectively. Due to the ALD growth mechanism, the film is a HfO_2-$HfLa_xO_y$ periodic structure in which La just interacts with a limited thickness of HfO_2, and La-free layers mainly composed of HfO_2. The presence of periodic HfO_2 thin interval layers adds an extra advantage in amorphous stabilization during high temperature annealing over that found for homogeneous $HfLa_xO_y$ mixtures and less overall La is required. Therefore ALD incorporating La is a potential method to grow amorphous HfO_2-La_2O_3 high-κ dielectric thin films.

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