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 lower WVTR values of ~6.5 x 10^-7 g/m^2/day for single Al2O3 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 x 10^-7 g/m^2/day at 70°C/28% RH with an Al2O3 ALD film thickness of 25 nm. This is the lowest WVTR value measured at elevated temperature for a single layer barrier film.

The Al2O3 ALD barriers are also deposited directly on the Ca films. This configuration allows the Ca test film to visualize the defects in the ALD 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 Al2O3 ALD film. The experiments demonstrate that the calcium oxidation is dominated by a few pinhole defects. The WVTR value of ~2 x 10^-7 g/m^2/day is consistent with several defects per cm^2 in the Al2O3 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 TiO2 on Si (100) and GaAs (100) Surfaces. T. Gougousi, J.W. Lasics, UMBBC, 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 ~6 Å/cycle by High Resolution Transmission Electron Microscopy (HRTEM) and spectroscopic ellipsometry, and Rutherford Backscattering measurements indicate steady state Ti atom coverage of 1.4x10^15 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 ~26 Å 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 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 H2O2/GaAs interface, which is very different but similar ALD chemistries that utilize amide precursors (TEMAH and TDMAH). 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]

3:00pm TF2-TuA4 Self-limiting Deposition of Anatase TiO2 for Photocatalytic Applications. N.G. Kubala, C.A. Holden, Colorado School of Mines
Titanium dioxide thin films were deposited using pulsed plasma-enhanced chemical vapor deposition at low temperature (T < 200 °C). Self-limiting deposition (~1 Å/cycle) was accomplished via simultaneous delivery of TiCl4 and O2. TiCl4 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 TiCl4 exposure, plasma power, and substrate temperature. Crystallization behavior observed at substrate temperatures as low as 120°C. Depositions at higher 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.

3:40pm TF2-TuA7 In situ X-ray Photoelectron Spectroscopy for the Study of Initial Stages of TiO2 ALD on Silicon. R. Methaapanon, Stanford University
Titanium dioxide (TiO2) is one of the widely studied atomic layer deposition (ALD) systems due to its outstanding electrical and optical properties that are suitable for a variety of applications. The properties of the deposited TiO2, 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, TiO2 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 (TiCl4) and water (H2O) are selected as precursors due to their molecular simplicity and broad operating temperature range that result in several achievable TiO2 phases. The initial growth at 100°C on two substrates - chemisorption 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. TiO2 growth on both SiO2 and H-Si surfaces exhibits linear behavior, as normally achieved by ALD, but the TiO2 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 TiO2 deposition on the SiO2 substrate suggest bond formation between titanium and silicon-bound oxygen at the interface. The data also suggest that some chlorine is trapped at the SiO2/TiO2 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 TiO2 using titanium tetrachloropropoxide (TTIP) as precursor. Operation 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 TiO2 surface for TTIP chemisorption were both surface carboxylates and –OH groups, identified in the 1450-1700 and 3400-3800 cm^-1 regions, respectively. Based on this observation, we conclude that plasma-assisted
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. Cavanaugh, 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. Alumcone MLD has been reported based on the reaction between trimethylaluminum (TMA) and ethylene glycol (EG). Zinccone 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 AlCH3* species. The sucrose then reacts with the AlCH3* 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 ZrO2 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 adsorbed H2O and O2. This reaction may be useful in gas barrier applications because the sugarcone film could serve as a chemical getter to adsorb any H2O 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. Moljojevic, B. Lee, R.M. Wallace, J. Kim, University of Texas at Dallas

Lanthanum based oxide (La2O3) having outstanding 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 to a formation of either La-hydroxide (La(OH)x) or La-silicate (La2SiO5) resulting in degradation of device properties. This problem may be useful in gas barrier applications because the sucrose film could serve as a chemical getter to adsorb any H2O that diffuses through the barrier.
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