

Thin Film

Room 2022 - Session TF-MoM

ALD and Applications I

Moderator: H. Kim, POSTECH, Korea

8:00am TF-MoM1 Spatially Controlled Nano-Scale Doping of Er@sup 3+@ in Y@sub 2@O@sub 3@ by Atomic Layer Deposition, J. Hoang, T.T. Van, M. Sawkar Mathur, University of California, Los Angeles; J. Bargar, Stanford Synchrotron Radiation Laboratory; B. Hoex, Eindhoven University of Technology, The Netherlands; W.M.M. Kessels, Eindhoven University of Technology, The Netherlands, Netherlands; M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands; R. Ostroumov, K. Wang, J.P. Chang, University of California, Los Angeles

We report in this work the utilization of radical enhanced atomic layer deposition (RE-ALD) to synthesize ultra thin films with controlled dopant incorporation. Er-doped Y@sub 2@O@sub 3@ is a potential waveguide core material for compact optical amplifiers because Y@sub 2@O@sub 3@ allows for incorporating of a higher concentration of Er and enables a compact geometry and a larger signal admittance angle. Extended X-ray Absorption Fine Structure (EXAFS) analysis showed that Er was in the optically active trivalent state in all samples, confirmed by their X-ray absorption near-edge spectroscopy. Modeling of the EXAFS data revealed that Er@sup 3+@ is coordinated with 6 O at 0.224 and 0.232 nm. The critical inter-ionic distance between two Er@sup 3+@ was determined to be 0.4 nm, thus setting an upper limit on the Er@sup 3+@ concentration in Y@sub 2@O@sub 3@ at about three orders of magnitude higher than the Er@sup 3+@ solubility limit in the conventional SiO@sub 2@ host. X-ray diffraction (XRD) and selected-area electron diffraction patterns revealed a preferential film growth in the [111] direction, showing a lattice contraction with increasing Er doping concentration, likely due to Er@sup 3+@ of a smaller ionic radius replacing the slightly larger Y@sup 3+@. The optical properties of Er@sup 3+@ ions incorporated in Y@sub 2@O@sub 3@ were investigated by using cavity ring-down spectroscopy (CRDS), and the peak absorption cross section of Er@sup 3+@ in Y@sub 2@O@sub 3@ at 1.53- μ m was estimated to be $\sim 2.0 \times 10^{-20}$ cm@sup 2@, about two times of that for Er@sup 3+@ in SiO@sub 2@. This is consistent with our previously reported larger effective absorption cross section of Er@sup 3+@ based on the photoluminescence yield as a function of the pump power. An important implication of this higher absorption cross section is that the population inversion can be achieved at a lower pump power and hence higher pumping efficiency.

8:20am TF-MoM2 MnO@sub 2@ and MgO Atomic Layer Deposition Using Bis(Ethylcyclopentadienyl) Precursors and H@sub 2@O, B.B. Burton, F.H. Fabreguette, D.N. Goldstein, S.M. George, University of Colorado at Boulder

The atomic layer deposition (ALD) of manganese oxide (MnO@sub 2@) and magnesium oxide (MgO) was studied using Fourier transform infrared (FTIR) spectroscopy and quartz crystal microbalance (QCM) measurements. MnO@sub 2@ ALD was performed at temperatures between 100-300°C using sequential exposures of Mn(CpEt)@sub 2@ [bis(ethylcyclopentadienyl)manganese] and H@sub 2@O. MgO ALD was performed at temperatures between 125-400°C using sequential exposures of Mg(CpEt)@sub 2@ [bis(ethylcyclopentadienyl)magnesium] and H@sub 2@O. The FTIR spectra were consistent with a loss of O-H vibrational features and a gain of C-H vibrational features during the M(CpEt)@sub 2@ exposure. The H@sub 2@O exposure produced a gain in O-H vibrational features and a loss of C-H vibrational features. The M-O bulk vibrational modes were also observed to grow in both cases between 500-1000 cm@super -1@. The QCM showed a maximum mass gain per cycle (MGPC) of 56 ng/cm@super 2@/cycle for MnO@sub 2@ at 150°C and a MGPC of 44 ng/cm@super 2@/cycle for MgO at 150°C. Both reactions were very efficient and required reactant exposures of only 2×10^{-5} L (1 L = 1×10^{-6} Torr s). The X-ray reflectivity (XRR) measurements were consistent with growth rate of ~ 1.1 Å/cycle at 150°C and ~ 1.41 Å/cycle at 150°C for MnO@sub 2@ and MgO, respectively. Based on thicknesses measured by XRR and the MGPC obtained by QCM, the density for the MnO@sub 2@ ALD films was 4.95 g/cm@super 3@ and the density for the MgO ALD films was 3.15 g/cm@super 3@. Transmission electron microscopy (TEM) was also performed after 40 AB cycles of MnO@sub 2@ ALD and 50 cycles of MgO ALD on ZrO@sub 2@ particles. In agreement with the growth rates obtained from the XRR measurements, the film

thicknesses observed by TEM were 54 Å and 85 Å for MnO@sub 2@ and MgO, respectively.

8:40am TF-MoM3 A New Fabrication Method of Nanostructural Materials by Using Selective Atomic Layer Deposition, M.M. Sung, Hanyang University, South Korea INVITED

We report a new fabrication method of nanostructural materials by using selective atomic layer deposition of thin films on patterned self-assembled monolayers and nanoporous templates. The patterned monolayers define and direct the selective deposition of thin films. This technique has been used successfully to deposit nanostructural materials on technologically important substrates including silicon and gold. Oxide nanotubes with diameter of 30 ~ 200 nm were successfully fabricated by this technique. It allows one-step processing for the fabrication of the freestanding oxide nanotubes. Sub-Ångstrom wall thickness controls in oxide nanotube@T structures can be achieved by this method. The nanostructural amaterials have been investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), water contact angles analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV spectrometer.

9:20am TF-MoM5 Mechanism of Al@sub 2@O@sub 3@ Atomic Layer Deposition Using Trimethylaluminum and Ozone, D.N. Goldstein, S.M. George, University of Colorado at Boulder

Al@sub 2@O@sub 3@ atomic layer deposition (ALD) is typically performed using trimethylaluminum (TMA) and H@sub 2@O. However, ozone can be used as the oxidant instead of H@sub 2@O. Ozone may lead to reduced Al@sub 2@O@sub 3@ leakage current for dielectric applications. Ozone may also purge faster than H@sub 2@O and lead to faster Al@sub 2@O@sub 3@ ALD. The mechanism of Al@sub 2@O@sub 3@ ALD using TMA and ozone is still under debate. To study the chemical species on the growing Al@sub 2@O@sub 3@ ALD surface, we have performed transmission FTIR vibrational spectroscopy investigations. High surface area ZrO@sub 2@ nanoparticles were utilized to obtain high surface sensitivities. The vibrational spectrum was recorded after each TMA or ozone reaction. The ozone generator produces 3.7 wt.% ozone in a 300 sccm O@sub 2@ flow in a viscous flow ALD reactor. Argon is utilized as the carrier gas to reduce reactive NO@sub x@ species. At the growth temperatures of 175 and 275°C, the FTIR results reveal that O@sub 3@ reacts with Al-CH@sub 3@ surface species produced by the TMA reaction and forms primarily formate groups and a mixture of methoxy and hydroxyl species on the surface. Production of formate groups may involve oxygen insertion into the Al-CH@sub 3@ bond to form methoxy species that are known to condense into formate groups at the reaction temperatures. The TMA then displaces the formate and methoxy groups and reforms Al-CH@sub 3@ surface species. FTIR difference spectra after TMA and O@sub 3@ reactions at 275°C are shown in the accompanying figure. These spectra are consistent with the loss and gain of formate and methoxy groups. The surface features are temperature dependent. At temperatures greater than 375°C, the FTIR vibrational spectrum reveals only formate groups on the surface.

9:40am TF-MoM6 Atomic Layer Deposition of Y@sub 2@O@sub 3@-Al@sub 2@O@sub 3@ Nanolaminate Thin Films and Compounds, J.C. Rowland, M. Davidson, P.H. Holloway, University of Florida

Alternating nano-scale thin films of Y@sub 2@O@sub 3@ and Al@sub 2@O@sub 3@ were grown by atomic layer deposition (ALD) with AlCl@sub 3@, Y(thd)@sub 3@, and H@sub 2@O precursors. The surface roughness was determined by AFM versus growth parameters such as substrate temperature (250-550°C), gas sweep time, etc. Growth rates of 0.4 nm/cycle were demonstrated. The composition was analyzed by Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), and shown to have low concentrations of impurities, especially Cl from the Al precursors. The microstructure and crystallinity / amorphicity were characterized using cross-sectional transmission electron microscopy (TEM), and X-ray diffraction (XRD). These data are interpreted in terms of the layer-by-layer ALD growth mode and compared to the properties of a single oxide film of Y@sub 2@O@sub 3@ or Al@sub 2@O@sub 3@. Solid state diffusion during post-growth annealing was investigated for forming various Y@sub 2@O@sub 3@-Al@sub 2@O@sub 3@ compounds such as Y@sub 2@Al@sub 5@O@sub 12@ (YAG), YAlO@sub 3@ (YAP), and Y@sub 4@Al@sub 2@O@sub 9@ (YAM), having cubic garnet, orthorhombic perovskite, and monoclinic structures, respectively.

Monday Morning, November 13, 2006

10:20am **TF-MoM8 Plasma Enhanced Atomic Layer Deposition of TiO₂ and HfO₂ as Plasma Source Configuration and Film Properties**, S.M. Rosznagel, IBM T.J. Watson Research Center; J. Joo, Kunsan National University, Korea; H. Kim, POSTECH, Korea

Plasma enhanced atomic layer deposition has advantages over thermal atomic layer deposition method in deposition rate, deposition temperature window, film density and choice of precursors. The role of plasma can be summarized into two categories; selective dissociation of precursors and enhancement of nucleation site density. Four different configuration of high density plasma sources were developed and applied to deposit TiO₂ and HfO₂ on 200 mm Si wafers using TiIP (titanium isopropoxide) and TEMA (tetrakis ethyl methyl amido hafnium) as precursors. For reactants, oxygen and water plasma were used. In addition, these same materials were evaluated by thermal ALD in the same tool. Optical emission spectroscopy was used as a real time diagnostic tool. Thickness and refractive index uniformity was monitored by ellipsometry. Chemical composition was evaluated by XPS and RBS. TiO₂ was rather insensitive to the configuration of plasma sources; the distance to the wafer, or the size of the plasma sources. 2% of non-uniformity in thickness and refractive index was typically obtained from 1 inch diameter inductively coupled plasma source, which means radical dominant process both in abstraction and nucleation steps. Leakage current and C-V characteristics showed good results in higher film thickness than 3.5 nm of TiO₂. HfO₂/TiO₂ multilayer and Hf/Ti (1-x)O₂ films were deposited to seek good combination for gate stacks.

10:40am **TF-MoM9 Interface Properties of Hafnium Oxide Films Grown by Atomic Layer Deposition on Native, Chemical Oxide and H-Terminated Si Surfaces**, J.C. Hackley, L. Takacs, T. Gougousi, UMBC

A hot wall Atomic Layer Deposition flow reactor equipped with a Quartz Crystal Microbalance (QCM) has been used for the deposition of HfO₂ thin films using tetrakis-ethylmethylamino hafnium (TEMA) and HfO₂ as precursors. HfO₂ films were deposited on H-terminated Si, native oxide and Si₃N₄ chemical oxide. Spectroscopic ellipsometry and QCM measurements confirm linear growth of the films with a growth rate of ~1.2 Å/cycle at 250°C. The films composition and morphology was examined using XPS, FTIR, AFM and XRD. Films are nearly stoichiometric HfO₂ (O:Hf ~1.95) with bonded carbon content less than 3 at. % and the surface rms roughness is ~ 3% of the film thickness. A similar incubation period of ~15 cycles is found for all three starting surfaces and X-ray photoelectron emission spectroscopy shows no SiO₂ formation at the interface for deposition on the H-terminated Si surfaces. However, there is evidence for Hf-O-Si bonding and RTA inert anneals (2 min in Ar) at temperatures as low as 300°C destabilize the interface and lead to the formation of interfacial SiO₂. X-ray diffraction data indicate that the films start to crystallize upon anneals at 300°C. From the XPS and XRD data we conclude that initially the H termination of the surface and the as deposited amorphous HfO₂ network protect the interface from oxidation. However, once the film begins to crystallize then diffusion of moisture and impurity O₂ along the grain boundaries is enhanced resulting in the formation of interfacial SiO₂.

11:00am **TF-MoM10 Atomic Layer Deposition of Aluminium Silicate Films**, P.J. Evans, ANSTO, Australia; P.H. Mutin, Universite Montpellier, France; G. Triani, Z. Zhang, A. Atanacio, J. Bartlett, ANSTO, Australia

The ALD of silicate films has been the subject of several recent studies. Interest in these materials has been stimulated in part by research into suitable candidates for the high-k dielectric layer in future semiconductor devices. While the ALD of hafnium and zirconium silicates have figured prominently in work to date, other metal silicates, such as those of aluminium, have also been reported. The present study investigates the deposition of aluminium silicate films by means of the reaction between aluminium chloride (AlCl₃), tetramethoxysilane (TMOS) and water at temperatures in the range 200 - 300 °C. An in-situ quartz crystal microbalance (QCM) was used to monitor the growth process in real time. The results of these measurements indicated that a single AlCl₃/H₂O pulse sequence followed by 3 - 5 pulse sequences of TMOS/H₂O enhanced both the growth rate and amount of Si in the film. These conditions were then used to deposit films on silicon wafers for ex-situ characterisation with ellipsometry, SIMS and XPS. It was found that films with approximately equal amounts of Al and Si could be obtained with the above precursors at 250 °C. At lower temperatures, the film growth rate decreased rapidly to the extent that negligible growth occurred at 200 °C. This finding is similar

to that observed in other cases where ALD film growth has been found to depend on the effect of temperature on reaction kinetics. @FootnoteText@ @footnote 1@ Vainonen-Ahlgren, E.; Tois, E.; Ahlgren, T.; Khriachtchev, L.; Marles, J.; Haukka, S.; Tuominen, M.; Comp. Mater. Sci. 2003, 27, 65. @footnote 2@ Kukli, K.; Ritala, M.; Leskelä, M.; Sajavaara, T.; Keinonen, J.; Hegde, R.I.; Gilmer, D.C.; Tobin, P.J. J. Electrochem. Soc., 2004, 151, F98. @footnote 3@ Kang, S-W.; Rhee, S-W.; George, S.M. J. Vac. Sci. Technol. A 2004, 22, 2392. @footnote 4@ Brei, V.V.; Kasperskii, V.A.; Chuiko, A.A.; Russ. J. Appl. Chem. 1996, 69, 335. @footnote 5@ Lim, J.W.; Yun, S.J.; Lee, J.H.; Electrochem. Solid-State Lett. 2005, 8, F25.

11:20am **TF-MoM11 Structure and Electrical Properties of BN Atomic Layer Deposition Grown in a Quasi-static Viscous Flow Reactor**, R.K. Grubbs, Sandia National Laboratories

Boron nitride (BN) is a desired material due to its thermal, electrical and tribological properties. The ability to deposit certain phases of BN via atomic layer deposition (ALD) could potentially solve a number of materials issues related to packaging and to MEMS systems. This talk describes the deposition, materials characterization and resulting electrical properties of ALD grown BN at a deposition temperature of 480 °C. Initial work on the ALD of BN was performed by Ferguson and George using FT infrared spectroscopy on ZrO₂ particles. Their work determined that large reactant exposures were necessary to complete the ALD surface chemistry. To produce ALD films of BN, an ALD viscous flow reactor was run in a quasi-static mode to obtain the necessary exposures required to saturate the surface chemistry. NH₃ and two different boron precursors were used to make BN thin films. Both BCl₃ and B(CH₃)₃ precursors were successful at producing BN ALD. The resulting thin films were analyzed with depth profile Auger electron spectrometry and x-ray diffraction. The BN films were amorphous as grown and did not convert to a crystalline phase under rapid thermal annealing conditions. The BN ALD grew at a rate of 0.7 Å/cycle at the 480 °C reaction temperature. Electrical measurements were performed on the BN ALD thin films as a function of film thickness. The breakdown voltage, leakage current and dielectric constant were measured for each BN synthesis and compared. Although BN ALD is a time consuming process, it can provide amorphous, low dielectric constant, pinhole free films for potential electrical, and diffusion barrier applications. @FootnoteText@ @footnote 1@ J.D. Ferguson, A.W. Weimer, S.M George, Thin Solid Films 413 16 (2002).

11:40am **TF-MoM12 Plasma Controlled Atomic Layer Deposition for Sealing Pores in Low-k Materials**, Y.-B. Jiang, J.L. Cecchi, University of New Mexico; C.J. Brinker, Sandia National Laboratories

On a porous substrate, atomic layer deposition (ALD) takes place not only on the top of the substrate, but also penetrates into the internal porosity. For sealing the pores of a nanoporous low-k materials, it is important to prevent any deposition in the internal pores, which would alter the material's dielectric constant. Consequently, an approach capable of confining ALD to the top surface of the porous substrate is needed. We have developed such a method by combining ALD with plasma processing. The ALD process is carried out such that deposition reaction will not take place unless triggered by a plasma. TEOS and O₂ have been used as the precursors for SiO₂ ALD in a plasma-ALD reactor. Although both precursors will be incident on all exposed surfaces, including the internal pores, they are not reactive to each other unless triggered by active plasma radicals. Since the radicals in the plasma do not penetrate into the nanoporous matrix, no ALD will take place in the internal pores. Another approach we have developed is an ALD process for which adsorption can not proceed unless the surface is activated by plasma. Using TMCS (trimethyl chlorosilane) and H₂O vapor as SiO₂ ALD precursors, ALD proceeds via the cycle of TMCS/Ar purge/O₂-plasma/H₂O vapor/Ar purge. After each TMCS exposure, the sample surfaces are passivated with -CH₃ groups. Upon the following exposure of an O₂ plasma, -CH₃ groups on the top surface are removed, leaving the surface reactive to subsequent precursor adsorptions. But the internal pores remain passivated, since plasma cannot reach them. In this manner, ALD is also confined to the top surface of the porous substrate. We present transmission electron microscope (TEM) images that establish that the SiO₂ ALD thus obtained was a several-nm-thick pore-sealing layer conformally on the top of patterned nanoporous silica without filling the internal pores.

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