Thin Films
Room 306 - Session TF-TuM

Atomic Layer Deposition - Oxides

Moderator: H. Kim, Pohang University of Science and Technology, Korea

8:20am **TF-TuM1 Atomic Layer Deposition of Titanium Oxide Thin Films using O@sub 3@ for MIM Capacitor of Next Generation Memory Devices**, ***S.K. Kim***, *K.M. Kim, C.S. Hwang,* Seoul National University, Korea

TiO@sub 2@ films were deposited using a travelling-wave type ALD reactor on a bare-Si (100) wafer, sputtered and ALD Ru, and sputtered Pt electrodes at a wafer temperature of 250°C. TiO@sub 2@ thin films was grown using Ti(OC@sub 3@H@sub 7@)@sub 4@ and O@sub 3@ as the precursor and oxidant, respectively. The dielectric constants of these TiO@sub 2@ films are 83 between 100 for the films on Ru electrodes. Crystalline structure of TiO@sub 2@ films on various substrates was investigated to understand the origin of higher k values of TiO@sub 2@ films on Ru substrates. XRD results of TiO@sub 2@ films on various substrates show that the TiO@sub 2@ films on Si and Pt substrates have anatase structure whereas the films on Ru substrates have rutile phase grains. This means that the growth of rutile TiO@sub 2@ is related to the kind of substrate. The growth of rutile TiO@sub 2@ on Ru substrate is induced by the formation of RuO@sub 2@, which has almost identical ion arrangements in its rutile structure, at the TiO@sub 2@/Ru interface. For the application of the material and ALD process to DRAM devices, TiO@sub 2@ films were grown on contact hole structured Ru electrodes and the dielectric properties of Ru/TiO@sub 2@/Ru 3-D capacitor were investigated. The conformity in film thickness and dielectric properties over the entire structured surface was confirmed by capacitance variation vs. hole surface area experiments. Also, addition of Al as an acceptor in TiO@sub 2@ films was tried to improve the leakage properties of TiO@sub 2@ films due to a rather high leakage current density of TiO@sub 2@ films. Although toxeq. of doped-TiO@sub 2@ films is smaller than that of undoped-TiO@sub 2@ films, leakage current density of doped-TiO@sub 2@ films is much lower than that of undoped-TiO@sub 2@ films.

8:40am **TF-TuM2 Characteristics of Atomic Layer Deposited TiO@sub2@ Films and its Photocatalytic Activity**, ***D.H. Kim***, *R. Pheamhom,* Chonnam National University, South Korea

Titanium dioxide has many attractive physicochemical properties and thus lends itself to various applications such as optical coatings for anti-reflection, high dielectric layers for electronic devices, biocompatible coatings for biomaterials, and photosensitive layers for photocatalysts and solar cells. In this work, tetrakis(dimethylamido) titanium (TDMAT) has been evaluated as a possible precursor for TiO@sub 2@ ALD using H@sub 2@O@sub 2@ as a counter-reactant. We have explored the effects of deposition temperature, reactants pulse and purging time on the film growth rate to optimize the ALD process for TiO@sub 2@ preparation using TDMAT. Self-limiting reaction was possible, as supported by saturated film growth rate and the linear property of the film growth depending on the number of cycles. Film growth rate, surface morphology, crystallinity, and conformality on the deposition temperature along with the photocatalytic activity of the ALD TiO@sub 2@ in decomposing methylene blue in aqueous solution will be presented.

9:00am **TF-TuM3 Atomic Layer Deposition of SrTiO@sub 3@ Films Having a High Thickness- and Cation-Composition Conformality Over a Severe Contact Hole Structure**, ***O.S. Kwon***, *S.W. Lee, C.S. Hwang,* Seoul National University, Korea

SrTiO@sub 3@ (STO) thin films were grown on Si wafer and Ru-coated Si wafers, respectively, by an atomic-layer-deposition (ALD) technique using conventional metal organic precursors, Sr(C@sub 11@H@sub 19@O@sub 2@)@sub 2@ (Sr(thd)@sub 2@) and Ti(Oi-C@sub 3@H@sub 7@)@sub 4@ (TTIP) as Sr- and Ti-precursors, respectively, with a remote-plasma activated and thermal H@sub 2@O vapor as oxidant. Although the each precursor exhibited ALD reaction with the remote-plasma activated H@sub 2@O vapor, STO exhibited quite different deposition behavior with the bubbling temperature of Sr(thd) @sub 2@. The cation stoichiometry of STO films was dramatically improved when the bubbling temperature of Sr(thd) @sub 2@ < 200°C (melting temperature of Sr(thd) @sub 2@) irrespective of the type of oxidants. Furthermore, cation composition conformality over the severe contact hole structure (0.13μm opening diameter with an aspect ratio of 8) was highly improved when the Sr(thd)@sub 2@ bubbling temperature was 180°C. The thickness step coverage over the entire contact hole was >95%, and the variation of cation composition was very small (< 3%). The different degree of oligomerization of Sr(thd)@sub 2@ with the bubbling temperature was supposed to be the reason for these phenomena. Electrical properties of STO films grown by ALD were highly dependent on the amount of oxidant. Leakage current density of STO films with lower oxidant supply was too high to measure the dielectric properties. The high leakage property was directly related to the binding energy shift into high binding energy direction of Sr 3d peak position in the XPS analysis. The leakage current density of STO films with sufficient oxidant was reduced and the binding energy shift of Sr 3d peak was reduced. Equivalent oxide thickness < 1nm and leakage current density < 10@super -6@A/cm@super 2@ at 1V were obtained by the optimized two step deposition and post-annealing processes.

9:20am **TF-TuM4 Selective Atomic Layer Deposition (ALD) for Fabrication of Metal and Oxide Nanotubes**, ***J.Y. Kim***, Kookmin University, Korea, Rep. of Korea; *D. Jeong, S. Won, H. Shin, J. Lee,* Kookmin University, Korea

In this study, we have fabricated various metal and oxide nanotubes using selective atomic layer deposition (ALD). We easily control the nanotubes shape and make high aspect ratio nanotubes by selective ALD using SAMs such as OTS(octadesyl-tetrachlorosilane). We avoid unnecessary deposition on top of nanotemplates such as poly-carbornate, which results in stand alone nanotubes without connection. The selective ALD is performed on sacrificial nanotemplates with pore sizes of 30 - 200nm. The template were commercial available polycarbonate (PC) and anodic aluminum oxide (AAO) with various hole sizes and thicknesses. After deposition, template was removed by wet etching. We successfully obtain metal (Cu,Co) and oxide(ZrO2,TiO2) single material nanotubes. In addition, metal/oxide double wall nanotubes are fabricated by sequential ALD process. We make metal oxide nanotubes and measure various properties using high resolution-transmission electron microscope (HR-TEM), field emission-scanning electron microscope (FE-SEM), selective area electron diffraction (SAED) patterns, X-ray diffractionmeter (XRD). We also characterize electrical properties of the nanotubes using conducting-atomic force microscope (AFM). The authors gratefully acknowledge the financial support through center for nanostructured materials technology by Korean ministry of science and technology (03K1501-02410).

9:40am **TF-TuM5 Laterally Graded Films and Multilayers Using Atomic Layer Deposition with a Slit Doser and Substrate Translation**, ***F.H. Fabreguette***, *S.M. George,* University of Colorado

Laterally graded multilayers have a bilayer spacing that continuously changes versus spatial position. These graded multilayer structures are important for x-ray collimation and x-ray focusing. Recently, optimized W/Al@sub2@O@sub3@ superlattices grown using atomic layer deposition (ALD) displayed an excellent x-ray reflectivity (XRR) of 96% at @lambda@=1.54 Å. To obtain laterally graded W/Al@sub2@O@sub3@ multilayers, the normal conformality of ALD must be circumvented by preventing ALD on the entire substrate. Laterally graded multilayers can be fabricated using a slit doser to localize reactant delivery in a viscous flow gas stream. The substrate is then translated relative to the slit doser with a magnetic linear translator. Since the viscous flow entrains the reactants and moves them downstream, substrate translation upstream of the slit doser prevents ALD on the entire substrate. A laterally graded Al@sub2@O@sub3@ ALD film was initially demonstrated by translating the substrate relative to the slit doser during Al@sub2@O@sub3@ ALD reaction cycles. Variable angle ellipsometry and XRR quantified a varying Al@sub2@O@sub3@ film thickness grown on a Si(100) wafer with a length of 6 inches. Changes in leakage current density and capacitance confirmed the Al@sub2@O@sub3@ thickness gradient. In addition, a laterally graded ZnO/Al@sub2@O@sub3@ multilayer was grown and characterized using XRR. The angle of the first Bragg peak revealed a bilayer spacing that changed as expected versus spatial position.

10:00am **TF-TuM6 Coating Nanoparticles by Atomic Layer Deposition in a Rotary Fluidized Bed Reactor: Al@sub 2@O@sub 3@ ALD on ZrO@sub 2@**, ***J.A. McCormick***, *A.W. Weimer, S.M. George,* University of Colorado at Boulder

Ultrathin and conformal Al@sub 2@O@sub 3@ films have been grown by atomic layer deposition (ALD) on ZrO@sub 2@ particles with diameters of 60 nm and 400 nm using sequential exposures of trimethylaluminum and H@sub 2@O. This Al@sub 2@O@sub 3@ ALD on gram-scale quantities of high surface area ZrO@sub 2@ nanoparticles was performed in a novel rotary fluidized bed reactor. The rotary fluidized bed reactor consisted of a stainless steel porous metal cylinder that rotated inside a vacuum system. The nanoparticles were contained inside the porous metal cylinder and the

gaseous reactants and products could easily diffuse through the porous walls without particle loss. A magnetically coupled rotary motion feedthrough rotated the porous metal cylinder and provided a fluidization-like mixing between the particles and the reactants. The Al@sub 2@O@sub 3@ ALD films were deposited on the ZrO@sub 2@ nanoparticles at 180°C with a growth rate of 1.8 Å/cycle. The composition of the Al@sub 2@O@sub 3@ ALD coating was verified using Auger electron spectroscopy, x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Transmission electron microscopy and BET surface area analysis were utilized to determine the conformality of the Al@sub 2@O@sub 3@ ALD coating and to check for particle coalescence. The Al@sub 2@O@sub 3@ ALD film uniformly coats the primary ZrO@sub 2@ particles and there was no evidence for any particle coalescence.

10:20am **TF-TuM7 The Atomic-Layer-Deposited HfO@sub 2@ Gate Dielectric Films; Chemistry of Interface and Electrical Performances**, *T.J. Park, M.J. Cho, S.H. Hong, M.H. Seo, J.H. Kim, J.H. Park,* ***C.S. Hwang,*** Seoul National University, Korea **INVITED**

HfO@sub 2@ thin films were deposited on HF-dipped Si wafers at temperatures ranging from 250 to 300°C using an atomic-layer-deposition technique with N-containing Hf[N(CH@sub 3@)@sub 2@]@sub 4@, Hf[N(CH@sub 3@)(C@sub 2@H@sub 5@)]@sub 4@ or Hf[N(CH@sub 3@)(@sub 2@H@sub 5@)]@sub 3@[OC(CH@sub 3@)@sub 3@] and H@sub 2@O or O@sub 3@ as the precursor and oxidant, respectively. A thin interfacial SiN@sub x@ layer was spontaneously formed at the HfO@sub 2@/Si interface during film growth. This interfacial SiN@sub x@ layer played a critical role in improving the thermal stability and interfacial trap (D@sub it@) property. D@sub it@ of < 5 x 10@super 10@ cm@super -2@eV@super -1@ near the mid-gap energy states was obtained from most of the process conditions but it usually suffer from the degradation by high temperature post-deposition annealing (PDA) at temperatures > 800°C. The adoption of O@sub 3@ oxidant reduced carbon impurity concentration and made the film more amorphous compared to the films grown using H@sub 2@O as oxidant. Although ozone was effective in reducing the impurity concentration, the higher concentration slightly deteriorated the dielectric performance. Investigation of the interface states using X-ray photoelectron spectroscopy revealed that the excessive oxygen incorporated during the film growth made the interfacial sub-oxide species (SiO, Si@sub 2@O@sub 3@ and silicate) and SiO@sub 2@ coordinate more with oxygen. This was further confirmed by the MOSFET performance comparison fabricated with HfO@sub 2@ gate dielectrics using different O@sub 3@ concentration. An electron effective mobility of ~ 65% of the MOSFET with SiO@sub 2@ as gate dielectric was obtained from the stoichiometric HfO@sub 2@ gate dielectric film. The effective mobility from the MOSFET with the oxygen excess HfO@sub 2@ film was only ~ 45 %.

11:00am **TF-TuM9 Atomic Layer Deposition for the Modification and Stabilization of Localized Surface Plasmon Resonance Nanosensors**, ***J.W. Elam,*** *M.J. Pellin,* Argonne National Laboratory*; A.V. Whitney, R.P. Van Duyne, P.C. Stair, G.C. Schatz, S. Zou,* Northwestern University

Noble metal nanoparticles serve as optical biosensors and chemosensors because of the localized surface plasmon resonance (LSPR) effect. The optical properties of LSPR sensors are strongly influenced by the size, shape and dielectric environment of the nanoparticles. Atomic layer deposition (ALD) can deposit dielectric films with atomic layer precision onto a variety of substrates including noble metals. Consequently, the optical properties of LSPR sensors can be tailored using ALD coatings. In this study, ordered arrays of Ag nanoparticles were coated with ALD Al@sub2@O@sub3@ and the resulting changes in the physical properties of the nanoparticles were explored. Initial experiments examined the nucleation and growth of ALD Al@sub2@O@sub3@ on flat Ag surfaces using quartz crystal microbalance and ellipsometry measurements. Surprisingly, these measurements demonstrated that the Al@sub2@O@sub3@ ALD proceeds on Ag without any nucleation delay. Next, ordered arrays of Ag nanotriangles fabricated using nanosphere lithography were coated using ALD Al@sub2@O@sub3@ at 50 °C. Optical absorption measurements revealed a 6 nm red shift in the LSPR peak for an Al@sub2@O@sub3@ thickness of only 1.6 Å. The LSPR peak continues to red shift with increasing Al@sub2@O@sub3@ thickness up to ~600 Å. These changes are explained well by theoretical analysis using finite element electrodynamics. The Ag nanotriangles were also examined using atomic force microscopy and scanning electron microscopy and these measurements demonstrated that the ALD Al@sub2@O@sub3@ conformally coats the nanotriangles while preserving their initial shape. Preliminary experiments reveal that thin ALD Al@sub2@O@sub3@ layers significantly improve the thermal stability of Ag nanoparticles while retaining strong Raman enhancement, suggesting that ALD coatings will broaden the range of applications for LSPR nanosensors.

11:20am **TF-TuM10 Atomic Layer Deposition (ALD) of Nickel Films Using Amidinate Precursors**, ***V.R. Pallem,*** *K. Kim, J.S. Park, R.G. Gordon,* Harvard University

Atomic layer deposition (ALD) of nickel thin films was demonstrated by using new nickel-amidinate precursors. Here we present a dozen nickel N,N'-Dialkyl-2-alkyl/aryl-amidinate derivatives as potential precursors for ALD. Their physical properties (volatility, thermal stability and chemical reactivity) were tuned by altering the alkyl groups. Nickel-bis(N,N'-di-tert-butylacetamidinate) showed the best overall properties as an ALD precursor. With NH@sub 3@ as a reducing agent at 270°C, self-limiting growth was achieved at a rate of 0.4 Å/cycle. Analyses of the deposited films showed only nickel. Nickel films grown on silicon nitride substrate had resistivity of 81 µ@ohm@-cm. Post-deposition annealing of nickel films on HF-last silicon showed the formation of nickel silicide.

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