Tuesday Afternoon, October 21, 2008

Thin Film
Room: 302 - Session TF-TuA

Applications of ALD II
Moderator: S.M. George, University of Colorado

1:40pm **TF-TuA1 ALD of High-k Gate Dielectrics on Si and Alternative Substrates**, ***J. Kim***, *H.C. Kim, B. Lee, A. Hande, E.M. Vogel, M.J. Kim, R.M. Wallace*, University of Texas at Dallas **INVITED**

For future high performance semiconductor device applications, it is critical to achieve a high quality gate dielectric with a high dielectric constant and excellent interface properties with semiconductor substrates such as GaAs, InGaAs and graphene in addition to Si. ALD has been considered as one of the most appropriate deposition techniques for high-k gate dielectrics without significant damage due to energetic particles and plasma. Due to its surface reaction nature, it is important to understand effects of reactants, such as precursors and oxidants, in conjunction with substrates on both interface and dielectric properties. Various materials characterization techniques including XPS, HRTEM, AFM, XRD, SIMS and RBS are used to investigate the physical properties of ALD derived metal oxide (Al_2O_3, HfO_2 and La_2O_3) thin films on various substrates. In particular, our in-situ XPS half-cycle study provides an insight on variation of chemical composition and binding status at the both interface and dielectric during the first few cycles.

2:20pm **TF-TuA3 ALD of High Dielectric Material LaMO3 (M = Y, Yb, Er) Using Metal Formamidinate Precursors**, ***H. Li***, *D.V. Shenai*, Rohm and Haas Electronic Materials, *R.G. Gordon*, Harvard University

The study of ultrathin gate dielectrics has recently gained great attention due to the technological need to replace SiO2 films in the metal-oxide-semiconductor field-effect transistors (MOSFETs).[1] According to the International Technology Roadmap for Semiconductors (ITRS),[2] the implementation of high-k gate dielectrics with a dielectric constant between 10 and 20 will be produced by leading manufacturers by 2008 in order to meet both low leakage current density and performance requirements. Ternary rare earth oxides are emerging as promising candidates for these applications. As shown in earlier report,[3] lanthanum lutetium oxide films (LaLuO3) obtained by pulsed laser deposition (PLD) technique showed a high dielectric constant of 32, very low leakage current density, remaining amorphous up to 1000 ºC and excellent performance. Similarly atomic layer deposition (ALD) of ternary rare earth oxide films such as GdScO3 or LaScO3 also demonstrated the potential for substituting current high k material.[4] However Lu and Sc elements are much less abundant in earth compared to other rare earth elements. So the precursors based on Lu or Sc can be extremely expensive to manufacture. Finding less expensive metals while maintaining those unique properties is urgent. Y, Yb and Er are three rare earth elements which are similar to Lu and Sc in ionic radii, but are much less inexpensive because of their natural abundance. In this presentation, we report the Y, Yb and Er precursors based on formamidinate platform, which has been demonstrated to offer higher vapor pressure and higher thermal stability of the sources than commercially available conventional precursors.[5] We will also report the ALD growth using H2O and O3 as co-reactants within the acceptable window of deposition temperatures. The resultant films will be characterized by AFM, XRD, and TEM.

[1]Wilk et al, J. Appl. Phys. 2001, 89, 5243.
[2]International Technology Roadmap for Semiconductors: 2007 edition.
[3](a) Lopes et al, Appl. Phys. Letts. 2006, 89, 222902.
[4](a) Kim et al, App. Phys. Letts. 2006, 89(13), 133512/1-133512/3. (b) Wang et al, AVS 55th International Symposium, Boston, MA, 2008.
[5]Li et al, 8th International Conference on Atomic Layer Deposition, Bruges, Belgium, 2008.

2:40pm **TF-TuA4 Electrical Properties of Plasma-Enhanced Atomic Layer Deposition $HfO_2/HfO_xN_y/HfO_2$ Gate Oxide**, ***W.J. Maeng***, *H. Kim*, POSTECH, Korea Republic

Nitrogen incorporation produces several benefits in the performance of high k gate oxides. However, since too much nitrogen incorporation at the interface of gate dielectric results in device degradation, the proper amount of nitrogen incorporation with precise depth profile control is desirable. In this study, the microstructure and electrical properties of plasma enhanced atomic layer deposition (PE-ALD) HfO_2 gate oxides with nitrided middle layer ($HfO_2/HfO_xN_y/HfO_2$) were investigated. The nitridation of the middle layer was carried out by two different in situ processes; PE-ALD using N/O mixture plasma (denoted as HfON) and PE-ALD HfN using hydrogen plasma followed by oxidation during the consequent HfO_2 deposition (denoted as HfONO). Significantly better electrical properties were obtained for HfONO than HfON in terms of hysteresis, equivalent oxide thickness, and reliability. In addition, high nitrogen incorporation up to 10 at% with improved thermal stability was achieved for HfONO sample. The experimental results will be discussed based on the atomic bonding configurations analyzed by X-ray photoemission spectroscopy.

3:00pm **TF-TuA5 Improvement of the Electrical Characteristics of Amorphous $LaAlO_3$ Films Made By Atomic Layer Deposition**, ***Y. Liu***, *H. Kim, J.J. Wang, R.G. Gordon*, Harvard University, *H. Li, D.V. Shenai*, Rohm and Haas Electronic Materials

Amorphous lanthanum aluminum oxide ($LaAlO_3$) films were deposited on hydrogen-terminated silicon substrates by atomic layer deposition (ALD) at 300 ºC. Capacitance-voltage measurements made from ALD $MoN/LaAlO_3/Si$ stacks showed humps especially at low frequencies, indicating traps for electrons or holes. Two sources of these traps were identified: impurities and oxygen vacancies. The number of traps was cut in half by careful purification of the La precursor to remove metallic impurities to below a total of 1 ppm. The remaining traps were effectively removed by adding an oxygen (O_2) exposure either after each ALD cycle or by a post-deposition O_2 treatment at 300 ºC, without affecting the dielectric constant (κ~15). The O_2 treatment also lowered the leakage current by an order of magnitude, to 1 mA cm^{-2} for films with EOT = 1.3 nm.

4:00pm **TF-TuA8 In-situ Conductance Measurements during Transparent Conductive Zinc Oxide Film Growth using Low Temperature Atomic Layer Deposition**, ***J.-S. Na***, *G.N. Parsons*, North Carolina State University

Zinc oxide has been extensively studied for applications such as solar cells, flat panel displays, gas sensors etc., and is considered as an alternative to indium tin oxide due to its low-cost, non-toxicity, and chemical and thermal stability. For the flexible device and TFT applications, low growth temperature (<150 ºC) or low carrier concentration ($<10^{18}$ cm^{-3}) is required. Here we report the low temperature atomic layer deposition (ALD) of zinc oxide using diethyl zinc and water as a precursor and reactant, respectively. We have developed a method to examine conductance in situ during ALD ZnO growth using two metal electrodes (Au/Cr) isolated by a thermally grown SiO_2 with a gap of 1 mm. Conductance was measured in situ during initial nucleation and steady state film growth at temperatures between 100-140 ºC. The growth rate, electrical resistance, surface morphology, and crystallininty were also studied ex situ as a function of growth temperature and ALD cycles. At 120 ºC the growth rate of ZnO ALD on SiO_2/Si was ~1.9 Å/cycles with ~3 cycles of incubation time and linear with the number of cycles. At 120 ºC with 0.1V applied, the current was below the detection limit ($<10^{-11}$ A) for the first 42 cycles. The current increased exponentially from 10^{-11} to 10^{-7} A between 43 and 50 cycles and followed by percolation to 10^{-5} A. From 70 to 200 cycles the current increased linearly from 10^{-5} to $5x10^{-4}$ A. Interestingly, the effect of each reactant exposure on the conductance of ZnO film during growth was quite different. Specifically at 120 ºC, both DEZ and water exposure dramatically increased the conductance of ZnO film at the exponential nucleation region. Meanwhile the DEZ exposure decreased and the water exposure increased the conductance of ZnO at the ohmic linear region. This technique shows a potential for in-depth understanding of the ALD ZnO growth process in situ and also how each reactant is involved in the defect formation related to the carrier concentration within the growing ZnO film.

4:20pm **TF-TuA9 ALD Noble Metal Oxides - Film Growth and Stability Studies**, ***M. Ritala***, *J. Hämäläinen, M. Heikkilä, K. Kukli, J. Niinistö, M. Kemell, M. Leskelä*, University of Helsinki, Finland

Noble metal oxide thin films gain interest over a broad range of application areas because of their attractive catalytic, optical, mechanical, electrical, and electrochemical properties. In integrated circuits, for example, high work function and structural similarity to high-k dielectrics make noble metal oxides potential electrode materials for capacitors and transistors. This presentation summarises our efforts in developing ozone based ALD processes for noble metal oxides. The consequences of the limited stability of noble metal oxides are also addressed using both high temperature XRD and chemical exposure experiments.

4:40pm **TF-TuA10 Increasing the Glass Cracking Resistance by Atomic Layer Deposition**, ***M. Putkonen***, *P. Soininen, M. Rajala,* Beneq Oy, Finland, *T. Mäntylä*, Tampere University of Technology, Finland

Infrared cut-off filters are used in CCD or CMOS sensors. Typically these filters are made onto separate glass sheets placed in front of the sensor. However, recently thinner and thinner glasses are used, for example in the wafer-scale integration, which causes increasing problems due to the cracking of the substrates. Cracking of the glass due to the nanometer-scale

Griffith-like flaws[1] is well known problem. These tiny flaws are usually in the range of 10-20 nm at the surface and they act as a starting point where bigger cracks start to develop. There are some available strenghtening approaches, based for example on the coatings made by solution methods.[2] However, these relative thick coatings may require high post annealing temperatures in order to obtain desired properties without sacrificing optical properties. In this study we introduce ALD technique for improving the crack resistance of the glass. Previously ALD has been employed for example for thin film deposition onto deep microelectronic trenches as well as for coating nanometer scale features. Since ALD is highly conformal surface-controlled coating method, it is expected that the film growth will closely follow the structural flaws of the glass surface. We have utilised TMA/H_2O and SAM24/O_3 processes and studied the mechanical and optical properties of films. For example, thin films were deposited onto soda lime and D263T glass substrates measuring from 20x50 mm^2 to 1200x1200 mm^2. Typical film thicknesses were in the range of 10-30 nm, but thicker coatings were also evaluated. Batches of smaller pieces (20x50 - 100x100 mm^2) were deposited in Beneq TFS 500 ALD system whereas bigger samples were evaluated in P400A, P800 and TFS 1200 systems. Depending on the sample size, glass thicknesses from 0.3 to 3 mm were evaluated. ALD processing of large area glass sheets were evaluated in terms of film uniformity and optical properties. Glass strength was evaluated against different thin film processing conditions and film thickness. According to the four point bending tests significant improvement on cracking strength were obtained by using ALD coatings.

[1] A. Griffith, The phenomena of rupture and flow in solids, Phil. Trans. Royal Soc., A221 (1920) 163.

[2] K. Endres et. al., Enhancement of fracture strength of cutted plate glass by the application of SiO2 sol-gel coatings, Thin Solid Films 351 (1999) 132.

5:00pm **TF-TuA11 In Situ Gas Phase Absorption Measurements During Hafnium Oxide ALD**, ***J.E. Maslar****, W.A. Kimes, J.T. Hodges, B. Sperling, D.R. Burgess, E.F. Moore*, National Institute of Science and Technology

In situ monitoring of atomic layer deposition (ALD) processes has the potential to yield insights that will enable improved efficiencies in film growth, in the development of deposition recipes, and in the design and qualification of reactors. In situ diagnostics potentially can be used to measure a number of parameters. Measuring precursor flux into the reactor is a relatively common application. However, such measurements are of limited value when trying to optimize deposition chemistry. Potentially more useful would be measurements of deposition precursor and product gas phase concentrations near the wafer surface. Such measurements would allow one to probe the properties of the near-surface thermal/gas velocity boundary layer that exists in many industrial ALD reactors. Since the properties of this boundary layer are strongly impacted by the state of the wafer surface, gas phase measurements in the boundary layer can provide information about the state of the wafer surface. In this work, semiconductor laser-based gas phase absorption measurements performed near the wafer surface are being investigated for use as in situ, real time diagnostics for ALD. The material system selected for investigation is hafnium oxide ALD using tetrakis(ethylmethylamino) hafnium (TEMAH) and water. Absorption measurements of water vapor were performed in the near-infrared (NIR) using a distributed-feedback (DFB) diode laser and employing a wavelength modulation detection scheme. Assuming complete reaction, the products of the TEMAH and water reaction are hafnium oxide and methyl-ethyl-amine, a volatile species under deposition conditions. Absorption measurements of methyl-ethyl-amine were performed in the NIR using an external-cavity diode laser (ECL) and employing an amplitude modulation detection scheme. In situ, time-resolved Fourier transform infrared spectroscopy measurements were used to compliment the laser-based measurements. Measurements were performed in a single-wafer, warm-wall reactor. Deposition precursor and product concentrations near the wafer surface were measured under a range of deposition conditions in an effort to correlate gas phase measurements with surface processes. The performances of the DFB laser-based and ECL-based measurement systems will be compared. In addition, efforts to model the observed concentration gradients using reactor-scale computational fluid dynamics models will be discussed.

5:20pm **TF-TuA12 Application of HRBS (High-resolution Rutherford Backscattering Spectrometry) to Elemental Depth Profiling of Advanced Gate Stack for Complementary Metal Oxide Semiconductor Devices**, ***C. Ichihara***, Kobe Steel, Ltd., Japan, *S. Yasuno,* Kobelco Research Institute Inc., Japan, *H. Takeuchi,* ATDF, *A. Kobayashi, S. Mure,* Kobe Steel, Ltd., Japan, *K. Fujikawa, K. Sasakawa*, Kobelco Research Institute Inc., Japan

Hafnium-based materials with high dielectric constant have started replacing conventional SiO_2-based materials as a gate dielectric for CMOS (complementary metal oxide semiconductor) devices at production level. Much of the effort has been made to develop gate stack structures without forming bulk defects and interface states, while maintaining compatibility with CMOS thermal budgets. It is thus very important to characterize the elemental depth profile of the gate stack accurately. As compared to conventional physical analyses such as SIMS, AES, XPS, and XTEM, High-resolution RBS (HRBS) has advantages in ultra-thin film characterization as it provides non-destructive and quantitative elemental measurements with a high depth resolution (up to sub-nm) and without special sample preparations. Using HRBS, we studied the change in elemental depth profile of ultra-thin HfSiO(N) films on Si. Three different interfacial layers (HF-last pre-cleaning; ~ 0.8 nm chemical oxide formed by wet cleaning; and ~1.4 nm thermally-grown SiO_2 film followed by plasma nitridation) were prepared prior to the growth of ~ 2 nm HfSiO film by ALD. For all of the as-deposited HfSiO film experiments, Si concentration was found to be slightly higher at the top surface than in the bulk HfSiO. It was also observed that the thickness of the interfacial SiO_x layer of the HF-last sample was similar to that of the sample with chemical oxide, indicating that the Si surface was oxidized during the ALD process. The samples were, then, spike-annealed in nitrogen ambient at 1070°C. After the annealing, the accumulation of the Si at the top surface was enhanced for all the three samples, indicating the upward diffusion of Si species from the HfSiO film. The interfacial layer of the sample with chemical oxide was found to be the thickest of all the three different surface preparations after the spike annealing. Furthermore, the change in nitrogen profile was studied for the samples fabricated in two different processes (plasma-nitridation vs. NH_3 annealing) for the HfSiO films prepared on chemical oxide. The HRBS spectra revealed the difference of the nitrogen desorption during the spike-anneal between the two nitridation processes.

Authors Index

Bold page numbers indicate the presenter

— B —

Burgess, D.R.: TF-TuA11, 2

— F —

Fujikawa, K.: TF-TuA12, 2

— G —

Gordon, R.G.: TF-TuA3, 1; TF-TuA5, 1

— H —

Hämäläinen, J.: TF-TuA9, 1
Hande, A.: TF-TuA1, 1
Heikkilä, M.: TF-TuA9, 1
Hodges, J.T.: TF-TuA11, 2

— I —

Ichihara, C.: TF-TuA12, **2**

— K —

Kemell, M.: TF-TuA9, 1
Kim, H.: TF-TuA4, 1; TF-TuA5, 1
Kim, H.C.: TF-TuA1, 1
Kim, J.: TF-TuA1, **1**
Kim, M.J.: TF-TuA1, 1
Kimes, W.A.: TF-TuA11, 2
Kobayashi, A.: TF-TuA12, 2
Kukli, K.: TF-TuA9, 1

— L —

Lee, B.: TF-TuA1, 1
Leskelä, M.: TF-TuA9, 1
Li, H.: TF-TuA3, **1**; TF-TuA5, 1
Liu, Y.: TF-TuA5, **1**

— M —

Maeng, W.J.: TF-TuA4, **1**
Mäntylä, T.: TF-TuA10, 1
Maslar, J.E.: TF-TuA11, **2**
Moore, E.F.: TF-TuA11, 2
Mure, S.: TF-TuA12, 2

— N —

Na, J.-S.: TF-TuA8, **1**
Niinistö, J.: TF-TuA9, 1

— P —

Parsons, G.N.: TF-TuA8, 1
Putkonen, M.: TF-TuA10, **1**

— R —

Rajala, M.: TF-TuA10, 1
Ritala, M.: TF-TuA9, **1**

— S —

Sasakawa, K.: TF-TuA12, 2
Shenai, D.V.: TF-TuA3, 1; TF-TuA5, 1
Soininen, P.: TF-TuA10, 1
Sperling, B.: TF-TuA11, 2

— T —

Takeuchi, H.: TF-TuA12, 2

— V —

Vogel, E.M.: TF-TuA1, 1

— W —

Wallace, R.M.: TF-TuA1, 1
Wang, J.J.: TF-TuA5, 1

— Y —

Yasuno, S.: TF-TuA12, 2