Thin Film
Room: Pecos - Session TF1-TuM

ALD: Dielectrics for Semiconductors
Moderator: H. Kim, Yonsei University, Korea

8:00am **TF1-TuM1 Feasibility of Wrinkle Free Graphene Process**, ***B.H. Lee****, C.H. Cho, S.K. Lim, S.Y. Lee, H.J. Hwang, Y.-G. Lee, U.J. Jung, C.G. Kang*, Gwangju Institute of Science and Technology, Korea **INVITED**

Graphene is an attractive material for advanced device applications due to its excellent electrical conductivity. Up to now, the best quality graphene in terms of electrical properties are obtained only from the graphene mechanically exfoliated from a natural graphite. Other processes such as a thermal graphitization of SiC and a precipitated graphene from metal films super saturated with carbon atoms did generate a good quality graphene in terms of Raman analysis. However, the morphology of graphene shows a high density of physical defects such as micro size wrinkles, island growth etc. For practical application of nanoscale device fabrication, global size wrinkles should be eliminated like a flat silicon substrate. Major sources of global defects in graphene are 1) a mismatch of thermal expansion coefficient between the graphene and the growth templates (metal, SiC etc), 2) a preferential out-diffusion or adoption of carbon along the grain boundary of metal. In this talk, a novel process that can detour these problems and generate a wrinkle free graphene will be discussed.

8:40am **TF1-TuM3 The Effects of Interfacial Organic Layers on the Growth of Thin Al_2O_3, HfO_2 and TaN_x Films by Atomic Layer Deposition**, ***K.J. Hughes****, S. Issacson, J.R. Engstrom*, Cornell University

One of the most poorly understood aspects of atomic layer deposition involves the initial stages of growth. As growth via ALD is almost always conducted on a substrate of different composition that the film being grown on top of it, there are often issues related to what are the best ways to initiate growth. Over the past few years we have been examining the use of interfacial organic layers (IOLs) as way to tailor the nucleation and growth of ALD thin films. Here, unlike essentially all work we have reported previously, we have conducted ALD using a conventional hot wall, viscous flow-type reactor, operating at pressures of ~ 1-100 mTorr. We focus here on the growth of two oxides: the benchmark Al_2O_3 and high-k HfO_2, and one nitride, TaN_x. As to the IOLs we consider one vapor phase deposited self-assembled monolayer, perfluorooctyltrichlorosilane (FOTS), which is expected to provide no active sites for ALD growth. We also consider a solution phase deposited polymer, poly(ethylene imine) (PEI), which possesses a high density of $–NH_2$ groups expected to act as active sites for growth. Concerning the latter IOL, from synchrotron x-ray reflectivity we confirm that PEI forms a thin (~ 7 Å) smooth film on the substrates we have examined. For ALD growth of Al_2O_3 on both bare SiO_2, and SiO_2 treated with PEI we observe linear growth, and no detectable incubation period. Growth on FOTS|SiO_2 on the other hand clearly exhibits an incubation period of ~ 15 cycles. Thus, for Al_2O_3, growth on unmodified SiO_2 and SiO_2 modified with PEI are indistinguishable. In contrast, growth of both HfO_2 and TaN_x is definitely perturbed by the presence of the PEI interfacial organic layer: compared to growth on unmodified SiO_2, growth on PEI |SiO_2 exhibits an incubation period of ~ 10 cycles for HfO_2, and > 40 cycles for TaN_x. A common question is what is the fate of the IOL? Concerning the growth of Al_2O_3, from *ex situ* angle-resolved x-ray photoelectron spectroscopy (ARXPS) we find that the elemental species associated with the IOL (F for FOTS, and N for PEI) are located at the IOL|Al_2O_3 interface, indicating the IOL has not migrated to the top surface during growth.

9:00am **TF1-TuM4 Property of Interfacial Layer Induced V_{FB} Shift in Al-related Gate Oxide Deposited by Remote Plasma Atomic Layer Deposition**, *H.T. Jeon,* ***H. Kim****, S. Woo, J. Lee, H. Lee*, Hanyang University, Republic of Korea

With the continuous dimensional scaling down of Si based devices has called for using high-k dielectrics to replace SiO2 or nitrided SiO2 as the gate oxide in CMOS devices. However, the untrollability of flatband voltage (VFB) is still a crucial issue for CMOS devices with high-k gate dielectrics. This undesirably flatband voltage shift is highly related to the interfacial defects, such as interface defect density, fixed charge density and oxygen vacancy. Therefore, it is significant to understanding the physical and chemical properties of the interface regions.

To grow thin films with excellent properties, plasma-enhanced atomic layer deposition (ALD) has been widely used as a thin film deposition method. PEALD commonly produces better quality of films at lower growth temperatures than dose thermal ALD because the required activation energy is provided by a plasma source. Some processes require the presence of radicals to enhance chemical reactions without having to use ion bombardment, as it can cause plasma-induced damage. Remote plasma ALD (RPALD), wherein the plasma is created in a remote chamber using RF power, was developed to meet these processing demands. The radicals generated in the plasma enter into the process chamber for deposition.

In order to understand the interfacial influence on the VFBshift in high-k based MOS structure, it is need to investigate the dependence of the VFB shift on the properties of interfacial layer. In this paper, to modify the Si surface, N2 plasma was treated on Si surface at RF powers of 100 W, 200 W and 300 W. The Al2O3 was deposited by remote plasma ALD at 250oC. The Pt/Al2O3/Si MOS structure was fabricated to investigate the impact of interfacial layer between Al2O3 and Si substrate on change in VFB. In addition, plasma was monitored by optical emission spectroscopy (OES). The physical and chemical properties of high-k dielectric films and interfacial layer were examined by XPS and AES.

We found that the nitrogen content at Si substrate increased during N2 plasma pre-treatment at high RF power which results in a negative shift of VFB. Therefore, the properties of the interfacail layer which are critical in determining the VFB are affected by N2 plasma pre-treatment.

9:20am **TF1-TuM5 Atomic Layer Deposited Pb(Zr,Ti)O_x Films Composited as Ferroelectric and Multiferroic Materials**, ***F. Zhang****, T.E. Quickel, Y.-C. Perng, S. Tolbert, J.P. Chang*, University of California, Los Angeles

Atomic layer deposition (ALD) of complex oxides is a viable method to tailor the composition and microstructure of the resulting thin films, thereby generating multi-functionality that is needed in various device applications. Another desirable feature of ALD is its ability to uniformly and conformally coat complex surface structures of high aspect ratios, making it possible to interface distinct materials to form composite materials that may show exciting properties, such as multiferroic behavior.

In this work, lead zirconium titanate (PZT) films were synthesized by depositing PbO, ZrO_2 and TiO_2 ALD layers with a sequence of (Pb-O)-(Ti-O)-(Pb-O)-(Zr-O). The deposition rate for PZT was approximately 0.7nm/cycle-sequence. The as-deposited materials were amorphous but crystallized into perovskite structure upon annealing to 950°C. The polarization properties found in the P-V measurements including remanent polarization (Pr), saturation polarization (Ps), and coercive field (Ec) are promising and are strongly affected by the ALD sequence which dictates the composition and structuring of the resulting thin film.

One example of the advantages of ALD produced PZT can be seen in our work on composite multiferroic materials, which can be created by coupling together nanoscale ferroelectric and ferromagnetic materials. In this work, mesoporous cobalt ferrite (CFO) thin films formed by block-copolymer templating methods with pores 14 nm in diameter were used as the ferromagnetic framework. Ultra-thin ALD PZT films were used to create a uniform and conformal coating over and on all CFO pore spaces and generate a nano-structured PZT-CFO hybrid material, as confirmed by scanning electron microscope (SEM), transmission electron microscope (TEM), and ultraviolet photoelectron spectroscopy (UPS) measurements. Superconducting quantum interference device (SQUID) magnetometry is underway to assess the multiferroic properties of this PZT/CFO composite, including both in-plane and out-of-plane saturation magnetization measurements after electrical poling and polarization voltage (P-V) measurements.

9:40am **TF1-TuM6 Y_2O_3 Atomic Layer Deposition from a Novel Process and its Integration in a Gate First Approach for 0.8 nm Equivalent Oxide Thickness**, ***C. Dubourdieu***, CNRS and IBM Research*, M.M. Frank, E. Cartier, J. Bruley, S.M. Rossnagel,* IBM T.J. Watson Research Center*, A. Kellock,* IBM Almaden Research Center*, V. Narayanan*, IBM T.J. Watson Research Center

A large part of the high-k dielectric stacks investigated for the replacement of the SiO_2 or Si_xO_yN gate oxide in metal-oxide-semiconductor (MOS) field-effect transistors consists of a Hf-based oxide or silicate deposited on top of an ultrathin interfacial SiO_2 layer. We report here the formation of yttrium lanthanum silicate in direct contact with silicon for the fabrication of MOS capacitors with a resulting highly competitive equivalent oxide thickness (EOT) of 0.8nm. Such a low EOT is remarkable as it is obtained with a non Hf-based dielectric and following a high-temperature gate first route. This result is achieved by integrating Y_2O_3 films grown on buffer layers by a novel atomic layer deposition process that combines an original yttrium precursor and an innovative liquid injection source.

The growth of Y_2O_3 thin films by ALD from $Y(EtCp)_3$ and water precursors will be presented. The yttrium precursor was introduced using a novel

delivery scheme consisting of a pulsed injection system from Kemstream®. The control of the growth as a function of various process parameters (precursor supply time, water purging time, temperature) was investigated. Film stoichiometry was determined by Rutherford backscattering spectrometry. The reactivity of $Y(EtCp)_3$ with water and the frontiers between ALD and CVD regimes will be discussed.

We describe MOS capacitors prepared from ALD-Y_2O_3 thin films deposited onto Si(p-type)/SiO_2(0.8 nm)/La_2O_3 (1 nm) structures. The Y_2O_3 thickness ranges from 1.5 to 3.5 nm. The metal gate electrode consists of 10 nm TiN and implanted polysilicon on top. The complete stack undergoes a high-temperature RTA at 1000°C for 5 s under N_2 for dopant activation in the poly-Si, which simulates gate first process of CMOS transistor fabrication. Finally, a forming gas anneal is performed at 475°C. The stack microstructure and composition were studied by transmission electron microscopy, electron loss spectroscopy and energy dispersive x-ray spectrometry. Interdiffusion reactions occur between SiO_2, La_2O_3 and Y_2O_3 layers upon the RTA and result in an yttrium lanthanum silicate film in direct contact with Si. The elemental distribution within the silicate layer will be discussed. C-V and I-V were performed on 10x10 μm^2 size capacitors in a frequency range of 1 kHz up to 300 kHz. EOTs as low as 0.8 nm were obtained for stacks with initially 3 nm Y_2O_3 deposited films. The leakage current density for such stacks is of $2.1x10^{-3}$ A/cm^2 at -1V. The formation of silicate enables an appropriate V_{FB}, which is tunable for nFET and pFET. Results obtained for stacks prepared from different buffer layers such as Al_2O_3 and HfO_2 will also be discussed.

10:40am **TF1-TuM9 Direct Liquid Injection Chemical Vapor Deposition of Nickel Ferrite and Barium Titanate Thin Films**, ***N. Li***, *A. Wang, A. Gupta, T.M. Klein*, University of Alabama

Multiferroic heterostructures, such as the ferromagnetic-ferroelectric bi-layered structures, have attracted a lot of attention due to their potential application in multifunctional devices. The simultaneous tunability of magnetic and electric fields in such structures is very useful for microwave and millimeter wave planar devices such as tunable phase shifters, resonators and delay lines. Growth of high quality and thick (10µm-100µm) ferromagnetic and ferroelectric thin films is an essential step to obtain satisfactory final devices. In this work, the growth of single crystal nickel ferrite (NFO, ferromagnetic) and barium titanate (BTO, ferroelectric) thin films with high growth rate by direct liquid injection chemical vapor deposition is investigated. The liquid precursor source for injection was prepared by dissolving corresponding metalorganic precursors into a solvent. In our case, $Ni(acac)_2$•PMDTA adduct (acac=acetylacetonate, PMDTA= N,N,N',N',N''-pentamethyldiethylenetriamine) and $Fe(acac)_3$ were dissolved in toluene as NFO precursor solution; $Ba(hfa)_2$•tetraglyme adduct (hfa=hexafluoroacetylacetonate) and $Ti(tmhd)_2(ipo)_2$ (tmhd= 2,2,6,6-tetramethyl-3,5-heptanedionato, ipo=isopropoxide) were dissolved in toluene as the BTO precursor solution. The as-prepared metal organic precursor solution was fed into a commercial vaporizer system through a liquid mass flow controller (10g/h range). Epitaxial growth of NFO and BTO thin films on MgO(100) were observed using X-ray diffraction. X-ray photoelectron spectroscopy showed the existence of trace amount of fluorine on the BTO surface. Scanning electron microscopy and atomic force microscopy showed the grain sizes to be around 100nm and the surface roughness around 20nm. The growth rates of both the NFO and BTO thin films are in the range of 0.5~1 µm/h under our experimental conditions.

11:00am **TF1-TuM10 Structure-Property Relationship in high-k, ALD Al-doped TiO_2 Films using Raman Spectroscopy**, ***L.C. Haspert***, *P. Banerjee, L. Henn-Lecordier, G.W. Rubloff*, University of Maryland

Thin film TiO_2 is a relatively high permittivity material with applications in electronic and energy devices. However, TiO_2 crystallizes easily, forming grain boundaries and creating current percolation pathways which increase leakage current and power consumption. Al-doped TiO_2 (ATO) increases the thermal stability of TiO_2, reducing leakage currents by suppressing phase transformation and limiting grain growth. To achieve the benefits of Al doping which retaining those of TiO_2, structure-property relationships must be optimized as a function of processing parameters.

Raman spectroscopy (RS), a highly sensitive technique for observing the evolution of nano-crystalline phases - their time evolution, volume fraction, defect states and stresses, is employed here to characterize ATO films grown by atomic layer deposition (ALD) and their correlation with electrical performance. 25nm TiO_2 thin films were deposited at 150°C in a Beneq TFS500 cross-flow ALD reactor by sequentially pulsing TDMAT and water precursors. Aluminum doping was controlled from 0 to 15 at% by introducing a single TMA / water pulse sequence at pre-determined intervals of multiple TDMAT/water pulse sequences during oxide growth, producing reproducible compositions estimated from their TiO_2 to Al_2O_3 pulse ratios. Following ALD the films were rapid thermal annealed (RTA) in an oxygen-rich environment ranging from 600°C to 1000°C from 5 to 300 sec.

The degree of crystallization was determined primarily through lineshape analysis of the Raman-active 144 cm^{-1} frequency mode. RS (and XRD) detected only the TiO_2 anatase phase, even at annealing temperatures where rutile formation was expected. RS data clearly shows the crystallization of TiO_2 with thermal anneal and that the crystallization onset shifts to higher temperatures with Al-doping while producing smaller grains. Pure TiO_2 films show a dielectric constant of 28.5 with high leakage currents (up to 10^{-3} A/cm^2). Annealed ATO films have a slightly lower dielectric constant (24) but leakage currents are dramatically reduced to ~ $1.0x10^{-7} A/cm^2$. The clear correlation between the microstructure measured by RS and the electrical performance of ALD TiO_2 and ATO thin films shows that RS can be a rapid, valuable monitor of thin film material nanostructure for correlation and optimization with electrical properties.

This work was supported by Laboratory for Physical Science, UMD

11:20am **TF1-TuM11 *In-situ* XPS and Half-Cycle Studies of Atomic Layer Deposited Al_2O_3 on Group-III Nitride Substrate for MOS-HEMT Applications**, ***P. Sivasubramani***, *T.J. Park, B.E. Coss, S. McDonnell, R.M. Wallace, J. Kim,* University of Texas at Dallas, *Y. Cao, D. Jena, H. Xing*, University of Notre Dame

Group-III nitride (III-N) technology has been widely used in optoelectronics, RF transistors and power switching due to a suitable bandgap, excellent transport properties, high breakdown field, low power losses, as well as the possibility of forming a heterojunction structure on low cost, large area substrate templates such as Si, sapphire, etc. [1] X-N alloy on Ga-N (where X = Ga, In, or Al) are expected to achieve high-speed switching performance due to a high carrier mobility of 2-D electron gas formed at the heterojunction interface. The introduction of a high-quality, ultrathin, atomic layer deposited (ALD) dielectric in between the metal and semiconductor has been shown to effectively decrease the diode leakage current without compromising the MOS-HEMT transfer characteristics. [2, 3] The evaluation of interfacial and bulk bonding configurations as a function of ALD dielectric growth parameters could provide valuable information for III-N device application. Therefore, in this work, we have investigated the growth, interfacial, and bulk properties of ALD Al2O3 dielectric on top of Ga-N on top of a low-cost sapphire template. Immediately after surface preparation, the samples were loaded in an ultra high vacuum (UHV) custom tool which has an integrated x-ray photoelectron spectroscopy (XPS), ALD, and a UHV transfer tube for in-situ analysis of ALD half-cycle reactions with the III-N substrate. The surfaces were pre-cleaned using atomic H cleaning and/or solvent-wet chemical cleaning. XPS of III-N substrates indicates that a small, higher oxidation state component, possibly a hydroxide or an oxynitride (e.g. Ga-O-N) exists on the as-grown surface. The hydroxide and residual carbon components on the clean substrate and during the half-cycle reactions are simultaneously monitored. Significant charging of the semiconductor during XPS is circumvented by using a doped substrate along with suitable charge references. ALD half-cycle studies of the TMA (tri-methyl aluminum)/water and TMA/O3 reactions on the III-N surface will be presented. References: [1] Phys. Status Solidi C 6, No. 6, 1361 (2009) [2] Appl. Phys. Lett. 86, 063501 (2005) [3] IEDM09-15

11:40am **TF1-TuM12 Defect Mechanisms for Chlorosilane Based Self-Assembled Monolayers**, ***S. Miller***, *A.J. Muscat*, University of Arizona

Self-aligning manufacturing processes could allow smaller device structures to be made as well as significantly reduce the number of manufacturing steps required. By utilizing selective chemistry it is possible to control where growth occurs for many different materials. Self assembled monolayers (SAMs), such as octadecyltrichlorosilane (OTS), have been used to inhibit the atomic layer deposition (ALD) of materials spanning from high-k dielectrics to metals such as Ir or Pt. By tailoring the selective chemistry, it is possible to chemically activate and deactivate the surface for multiple materials. SAMs such as 3-mercaptopropyltriethoxysilane have been used to attach a variety of nanoparticles where desired, and when combined with other SAMs such as OTS can prevent adsorption or deposition where undesired. Simple patterning techniques such as photolithography, AFM lithography, or electron lithography can be combined with selective chemistries to allow high resolution spatial control over the growth and deposition of materials. One limitation of this technology is the long time scales required to fully deactivate deposition using SAMs, which are on the order of 48 hours. Molecular defects such as water in the SAM, unblocked hydroxyl groups, exposed Si-O bonds, misaligned boundaries between forming SAM islands, or polymerized SAM molecules in the SAM layers also leads to an eventual failure point for deposition deactivation. We found that they can be largely eliminated by forming the SAM on a uniformly hydroxylated surface, using a chloroform rinse step, and removing any polymerized or physisorbed SAM molecules from the surface during SAM formation. Using $TiCl_4$ as a probe for defect

sites, the level of each defect type has been determined. The number of defects sites on the surface on a typical OTS SAM is on the order of 10^{12} molecules/cm^2. 1/3rd of the defects are associated with the physisorbed SAM molecules. Of the other 2/3^{rds} of SAM defects nearly half are unblocked hydroxyl groups while the other half are likely open Si-O bonds at grain boundaries. Water has been shown not to be a contributing cause for nucleation of deactivation failure. TiO_2 deposition from a $TiCl_4$ and H_2O ALD process at 170°C has been deactivated for at least 100 cycles after treating for only 4 hours in 10mM OTS in toluene solution, as long as the sample is removed every hour and rinsed. The extraction step removes unwanted SAM molecules and exposes open surface areas allowing for new SAM molecules to quickly fill the gaps. These improvements in both the quality and the time scale of SAM formation could it feasible to begin incorporating these technologies into manufacturing.

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