

Tuesday Morning, November 1, 2011

Electronic Materials and Processing Division

Room: 210 - Session EM+TF-TuM

High-k Dielectrics for MOSFETs Part 1

Moderator: R.M. Wallace, University of Texas at Dallas

8:20am **EM+TF-TuM2 In Situ TMA Pre-Treatment Study of GaAs and In_{0.53}Ga_{0.47}As Surfaces**, B. Brennan, D.M. Zhernokletov, H. Dong, R.V. Galatage, J. Kim, E.M. Vogel, R.M. Wallace, University of Texas at Dallas

One of the major issues preventing the integration of high mobility III-V semiconductors into next generation CMOS devices is the formation of high levels of interfacial defects at the high-k/III-V interface. These can have the effect of pinning the Fermi level and preventing optimal operation of the devices. Engineering the interface between these materials therefore becomes of critical importance to try and reduce the defect density. Identification of the individual defects however is not a trivial matter with correlation between electrical data and physical measurement techniques rarely seen. This study aims to investigate the effect of *in-situ* chemical treatments prior to Al₂O₃ deposition on (NH₄)₂S treated GaAs and InGaAs surfaces, in terms of both physical characterization by X-ray photoelectron spectroscopy (XPS) and electrical measurements from MOS capacitors.

The reduction of interfacial oxides through a "clean up" effect by a ligand exchange mechanism with the tri-methyl aluminum (TMA) precursor for atomic layer deposition (ALD) of Al₂O₃ is well known, [1,2] however little work has been carried out to optimize this process and determine whether variations in the effect are seen as a result of changes in the number of TMA cycles or pulse time prior to oxide deposition. Variations in the presence of arsenic surface features, (i.e. As-As bonding or surface dimers) come under particular focus. The effect of post deposition annealing is also investigated specifically in terms of the potential role hydrogen could play in passivating defects at the interface. [3]

[1] C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, H. C. Kim, J. Kim, R. M. Wallace, *Appl. Phys. Lett.* 92, 071901, (2008)

[2] B. Brennan, M. Milojevic, H.C. Kim H.C, P.K. Hurley, J. Kim, G. Hughes, R.M. Wallace, *Electrochem. Solid-State Lett.*, 12, 6, (2009)

[3] H. D. Trinh, E. Y. Chang, P. W. Wu, Y. Y. Wong, C. T. Chang, Y. F. Hsieh, C. C. Yu, H. Q. Nguyen, Y. C. Lin, K. L. Lin, M. K. Hudait, *Appl. Phys. Lett.* 97, 042903 (2010)

8:40am **EM+TF-TuM3 Half-cycle Atomic Layer Deposition Studies of HfO₂ on the GaSb(001) Surface**, D.M. Zhernokletov, H. Dong, B. Brennan, J. Kim, R.M. Wallace, University of Texas at Dallas

Since GaSb(001) is a candidate surface channel material for p-MOSFET and an interfacial passivation layer for buried channel quantum well and tunneling FETs (GaSb static dielectric constant of ~ 16), it is necessary to understand its interface with high-κ dielectric materials which would act as gate dielectrics in these devices[1]. An *in-situ* half-cycle atomic layer deposition/X-ray photoelectron spectroscopy (ALD/XPS) study is conducted in order to investigate the evolution of the HfO₂ dielectric interface with the GaSb(001) surface after sulfur passivation procedures and HCl etching designed to remove the native oxides. Monochromatic XPS is used to examine the surfaces following the various surface treatments and then without breaking vacuum, after each individual ALD pulse of tetrakisdimethyl-amino-hafnium (TDMA-Hf) and deionized water (DIW) precursors (i.e. single TDMA-Hf pulse/XPS scan; single DIW/XPS scan; etc.) for two full cycles and finally after 1 nm of HfO₂ deposition to determine whether there is any "clean up" effect of the native oxides due to the ALD process. The various surface preparation techniques are compared to determine which is more effective at minimizing native oxides. The behavior of the sulfides and the effect of HCl surface cleaning procedure upon HfO₂ deposition are discussed as well as a comparison to previous results from half cycle Al₂O₃ deposition on GaSb [2]. This work is supported by the Semiconductor Research Corporation FCRP MSD Focus Center, the Nanoelectronics Research Initiative and the National Institute of Standards and Technology through the Midwest Institute for Nanoelectronics Discovery (MIND), and the NSF (ECCS-0925844).

[1] A. Nainani, T. Irisawa, Z. Yuan, Y. Sun, T. Krishnamohan, M. Reason, B.R. Bennett, J.B. Boos, M. Ancona, Y. Nishi, K.C. Saraswat, International Electron Devices Meeting, (IEDM) Tech. Dig. (2010).

[2] S. McDonnell, D. M. Zhernokletov, A. P. Kirk, J. Kim, and R. M. Wallace. *Applied Surface Science Letters*, submitted (2011).

9:00am **EM+TF-TuM4 Remote Phonon and Surface Roughness Limited Universal Electron Mobility of In_{0.53}Ga_{0.47}As Surface Channel MOSFETs**, E.M. Vogel, A.M. Sonnet, R.V. Galatage, University of Texas at Dallas, P.K. Hurley, E. Pelucchi, K. Thomas, A. Gocalinska, Tyndall National Institute, J. Huang, N. Goel, G. Bersuker, SEMATECH, W.P. Kirk, C.L. Hinkle, University of Texas at Dallas

INVITED
The inversion layer electron mobility in n-channel In_{0.53}Ga_{0.47}As MOSFETs with HfO₂ gate dielectric with several substrate impurity concentrations (~1×10¹⁶ cm⁻³ to ~1×10¹⁸ cm⁻³) and various surface preparations (HF surface clean, (NH₄)₂S surface clean and PECVD a-Si interlayer with a HfO₂ gate dielectric) have been studied. The peak electron mobility is observed to be strongly dependent on the surface preparation, but the high field mobility is observed to be almost independent of the surface preparation. A detailed analysis of the effective mobility as a function of electric field, substrate doping, and temperature was used to determine the various mobility components (surface roughness, phonon, and coulombic scattering limited mobility components). For the substrates with high doping concentration, the electron mobility at low vertical electric field is dominated by Coulomb scattering from the substrate dopants, whereas, for lower substrate doping the Coulombic scattering is dominated by the disorder induced gap states. Low temperature measurements were used to determine the surface roughness scattering and phonon components. The results show that room temperature mobility of In_{0.53}Ga_{0.47}As surface channel MOSFETs with HfO₂ gate dielectric at high electric field is limited primarily by remote phonons whereas the Al₂O₃ gate dielectric is limited by surface roughness scattering.

9:40am **EM+TF-TuM6 Structural Characterization of Ultra-thin High-k Gate Oxide Films through a Multi-technique Approach**, E.J. Bersch, J.D. LaRose, I.B. Wells, University at Albany, S.P. Consiglio, R.D. Clark, K.N. Tapily, G.J. Leusink, TEL Technology Center, America, LLC, A.C. Diebold, University at Albany

High-k HfO₂-based gate oxides have recently been put into production in CMOS-based integrated circuits, and their future use in this capacity depends on how well they can continue to be downscaled. To this end, efforts to increase the dielectric constant (k) of HfO₂-based gate oxides are ongoing. Recent work has shown that by tailoring annealing procedures, k values for HfO₂ films of greater than 30 have been obtained.¹ These higher k values for HfO₂ occur for the metastable tetragonal and cubic crystalline phases, while the thermodynamically preferred monoclinic phase has a lower k value (~20). To evaluate the crystalline structure of ultra-thin (< 100 Å) HfO₂ films which have undergone various annealing treatments, we used several techniques, including grazing incidence in-plane X-ray diffraction (GIIXRD), X-ray and UV photoemission spectroscopy (XPS and UPS, respectively) and spectroscopic ellipsometry (SE). GIIXRD measurements showed that ~60 Å HfO₂ films grown with a sequence of depositions and anneals (so-called DADA process²) were monoclinic, while those which were post deposition annealed (PDA) were in a mixture of monoclinic and either tetragonal or orthorhombic phases. Pole figure measurements of these films showed that the DADA film had a monoclinic (-111) fiber texture, while the PDA film was randomly oriented. For HfO₂ films with thicknesses of ~25 Å, GIIXRD measurements showed that DADA films were tetragonal or orthorhombic, while PDA films were also tetragonal or orthorhombic, but also possibly with a monoclinic component. XPS and UPS measurements of the valence bands of HfO₂ films were found to be useful in distinguishing between crystalline and non-crystalline films, but were not useful in distinguishing between crystalline phases.³ SE has been shown to be useful in identifying crystallinity in HfO₂ through a feature that appears in the HfO₂ extinction coefficient curve at the absorption edge. We have observed this absorption edge feature for films that were crystalline and strongly monoclinic, but not for films that were only weakly crystalline or mostly non-monoclinic, in keeping with previous work.⁴

References:

[1] S. Migita, *et al.*, 2008 Symposium on VLSI Technology, 152-153(2008).

[2] R.D. Clark, *et al.*, *ECS Trans.*, **35(4)**, 815-834 (2011).

[3] S. Toyoda, *et al.*, *J. Appl. Phys.*, **97**, 104507 (2005).

[4] J. Schaeffer, *et al.*, *J. Electrochem. Soc.*, **150** (4), F67 (2003).

10:40am **EM+TF-TuM9 Research Advances on III-V and Ge MOS/MOSFETs Beyond Si CMOS**, *T.D. Lin, M.L. Huang, Y.C. Chang, W.C. Lee*, National Tsing Hua University, Taiwan, Republic of China, *T.W. Pi*, National Synchrotron Radiation Research Center, Taiwan, Republic of China, *J. Kwo*, National Tsing Hua Univ. and National Taiwan Univ., Taiwan, Republic of China, **M. Hong**, National Tsing Hua University, Taiwan, Republic of China **INVITED**

Metal-oxide-semiconductor (MOS) and MOS field-effect-transistors (MOSFETs) of high k dielectrics on high carrier mobility channels of InGaAs and Ge have been feverishly studied, as they are now strongly considered for technologies beyond Si complementary MOS (CMOS) integrated circuits (ICs). The post Si CMOS research is now facing unprecedented challenges in materials and physics, as key material/electrical/processing issues have to be met/solved in order to realize the new advanced devices; these include equivalent oxide thickness (EOT) < 1 nm, interfacial density of state (Dit) $\leq 10^{11}$ eV $^{-1}$ cm $^{-2}$, high-temperature thermal stability for self-aligned process, low parasitic, and integration with Si. Using *in-situ* ultra high vacuum (UHV) and *in-situ/ex-situ* atomic layer deposited (ALD) high k 's of Ga $_2$ O $_3$ (Gd $_2$ O $_3$), Al $_2$ O $_3$, and HfO $_2$ on InGaAs and Ge, this research group has made advances in achieving an EOT of 0.5 nm, Dit of low 10^{11} eV $^{-1}$ cm $^{-2}$ (with a flat distribution versus energy within the semiconductor bandgap), and high-temperature stability of the MOS structures (rapid thermal annealing to 800-900°C and 500-600°C for the high k 's/InGaAs and /Ge, respectively). Atomic manipulation to perfecting the high k 's/InGaAs and /Ge interfaces is the key for the above achievements. Probing of the interfaces and gaining insightful understanding of the electronic properties was made possible using our uniquely designed experiments of *in-situ* synchrotron radiation photoemission. High-performance self-aligned inversion-channel high k 's/InGaAs MOSFETs in achieving record-high drain currents and transconductances, and record-low sub-threshold swings, and high k 's/Ge MOSFETs without employing interfacial passivation layers will also be discussed.

11:20am **EM+TF-TuM11 SiO $_2$ Interlayer Thickness Dependence of the Density and Polarity of Charges in Si/SiO $_2$ /Al $_2$ O $_3$ stacks**, *N.M. Terlinden, G. Dingemans, M.M. Mandoc, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

In this contribution, we investigate the influence of the SiO $_2$ thickness on the *density* and *polarity* of built-in charges in SiO $_2$ /Al $_2$ O $_3$ stacks deposited on Si(100). Such charges lead to the development of a space-charge region (SCR) in the Si at the dielectric interface, having consequences such as flat band voltage shifts in MOS devices and electric-field induced passivation in optoelectronic devices like solar cells. We have employed the nonlinear optical technique of second-harmonic generation (SHG) to probe the Si(100) SCR electric field through the effect of electric-field-induced SHG (EFISH). Using this non-intrusive and contactless technique we found previously that the built-in charge density at the SiO $_2$ /Al $_2$ O $_3$ interface is independent of the Al $_2$ O $_3$ thickness down to ~ 2 nm.¹ Here we report on the influence of the interfacial SiO $_x$ layer, present between the Si(100) substrate and the atomic layer deposited (ALD) Al $_2$ O $_3$ film, addressing the origin, density, and polarity of the charges. For this reason, we have synthesized SiO $_2$ /Al $_2$ O $_3$ stacks with intentionally grown SiO $_2$ interlayers having a thickness in the range ~ 1.4 -150 nm using various deposition methods (e.g. thermal oxidation, PECVD, ALD). Spectroscopic SHG measurements were carried out with a femtosecond pulsed Ti:sapphire laser tunable in the 1.33-1.75 eV photon energy range. From the obtained spectra we found that the charge density is highly influenced when increasing the SiO $_2$ thickness, dropping from 10^{13} to 10^{11} cm $^{-2}$, with the polarity switching from negative to positive. These measurements were confirmed by *C-V* measurements and surface voltage measurements employing corona charging of the stacks. On the basis of the observations the mechanism and consequences of charge trapping in Si/SiO $_2$ /Al $_2$ O $_3$ stacks will be addressed.

¹ Terlinden *et al.*, Appl. Phys. Lett. **96**, 112101 (2010)

11:40am **EM+TF-TuM12 Study of the Interface Barrier of Atomic Layer Deposited (ALD) Al $_2$ O $_3$ on GaN**, *M. Esposto, S. Krishnamoorthy, D.N. Nath, S. Bajaj, S. Rajan, T.-H. Hung*, Ohio State University

We report on the deposition and energy band diagram analysis of high-quality low-leakage Al $_2$ O $_3$ /GaN using atomic layer deposition. As GaN-based transistors are scaled to achieve higher frequency operation, atomic layer deposition techniques offer a promising way to achieve low leakage while scaling gate-to-channel distance. In addition, applications of GaN in power switching systems require ultra-low leakage that can be achieved using metal-insulator-semiconductor (MISHEMT) structures. In this work, we have made quantitative estimates of conduction band offsets and interface charge density.

MIS structures with varying oxide thickness were fabricated on an n+/n-GaN sample grown by RF plasma MBE on low dislocation density Lumilog

GaN templates. Three Al $_2$ O $_3$ layers of nominal 6 nm, 12 nm, and 18 nm were deposited by atomic layer deposition at 300°C, using trimethylaluminum (TMA) and H $_2$ O as precursors. The pre-deposition treatment of the surface consisted in a 10:1 HF-dip for 15s. All three samples were then annealed at 600°C in forming gas for 1min. A new ALD deposition procedure was also developed to achieve low leakage in these structures.

A quantitative analysis of the interface barrier of Ni/Al $_2$ O $_3$ /GaN capacitors was carried out to determine conduction band discontinuity, interface fixed charge and pinning effects. The I-V measurements show extremely low current density for thin dielectric films. A quantitative energy band diagram was estimated from capacitance voltage (C-V) measurements by extracting the apparent charge profiles of the MIS capacitors taking into account the spontaneous polarization in GaN and doping. The extracted flat-band voltages were -0.36 V, -1.55 V and -2.73 V for the 6 nm, 12 nm and 18 nm-thick oxide respectively. The hysteresis in the C-V profile for the 6nm-thick capacitor pointed out a D $_it$ charge density of approximately 5×10^{11} cm $^{-2}$ and higher for the thicker capacitors. This was because the deposition and post deposition annealing conditions were optimized for very thin oxide layers (~ 5 -6 nm). A linear relationship between the flat-band voltage and the oxide thickness was experimentally observed, indicating absence of Fermi-level pinning at the Al $_2$ O $_3$ /GaN interface. The conduction band offset at the Al $_2$ O $_3$ /GaN interface was calculated to be 2.66 eV. In addition, we estimate that a non-zero field of approximately 2 MV/cm exists in the oxide under flat band conditions in the semiconductor. This non-zero field is attributed to a fixed charge density at the Al $_2$ O $_3$ /GaN interface of 2.79×10^{13} cm $^{-2}$.

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