Electronic Materials and Processing
Room 312 - Session EM2-TuM
High-k Dielectric Characterization
Moderator: G. Wilk, ASM America

8:20am **EM2-TuM1 Characterization of High-@kappa@ Materials using High Resolution Ion Backscattering**, ***T. Gustafsson***, *E. Garfunkel, L.V. Goncharova, R. Barnes, D. Starodub,* Rutgers University **INVITED**

Understanding the thermodynamics and kinetics of film growth during fabrication of high-@kappa@ gate stacks is vital to establish atomic level control of interfacial layers and to minimize defects. Annealing such films in different atmospheres may lead to diffusion and reactions with significant consequences on the electrical properties. Ion beam methods, in particular medium energy ion scattering (MEIS), are non-destructive, high resolution (sub-nm) tools for quantitative characterization of buried layers and interfaces. An attractive feature is the possibility to use isotope tracing, which allows a study not just of the structures of such ultrathin films, but also of the processes responsible for their formation. We will discuss some key materials issues relevant to films and interfaces in next-generation highly-scaled CMOS gate stack structures as investigated using ion beams. As one example, we will contrast the behavior of Hf and Ce oxides on Si during annealing in an oxide atmosphere. The Hf based system shows evidence for oxygen exchange, which could be suppressed by mixing the oxide with SiO@sub 2@. Little SiO@sub 2@ interfacial growth was observed. This reaction saturates with time and appears to be enhanced after film recrystallization. Annealing in nitrogen results in reduced oxygen incorporation and exchange. In contrast, Ce silicates exhibit rapid interface growth upon oxygen exposure. Materials changes occur in the ultrathin films and at the various interfaces during growth and processing at elevated temperature that strongly affect device properties. Changes in oxide and silicate interface composition and thickness, phase mixing and crystallization within the film, and film decomposition will be discussed also for high-@kappa@ films on Ge and GaAs. In general the native oxides on these materials are less stable than those of Si, leading to different high-@kappa@ layered structures and interface composition.

9:00am **EM2-TuM3 Fermi Level Pinning at Re/HfO@sub2@ Interface and Effective Work Function of Re in Re/HfO@sub2@/SiO@subx@/n-Si Stack**, ***Y. Liang***, *J. Curless, C. Tracy, D. Gilmer, J. Schaeffer, D. Triyoso, P. Tobin,* Freescale Semiconductor Inc.

One of the challenges in metal/high-k/Si based CMOS devices is a need for a metal with work function aligned with the Si valence band edge (5.2 eV) for PMOS devices. While a number of metals have vacuum work functions equal or greater than 5.2 eV, their effective work functions in a MOS structure are often less than 5.2 eV due largely to Fermi level pinning in the metal/high-k/Si stack. We used x-ray and ultra-violet photoemission spectroscopy (XPS and UPS) in conjunction with capacitance-voltage (C-V) measurements to investigate Fermi level pinning in a Re/HfO@sub2@/SiO@subx@/n-Si stack. Evolution of the Re vacuum work function at different Re film thickness and the resulting band bending in HfO@sub2@ and Si were determined by in situ XPS and UPS techniques. Results showed that the Re vacuum work function reached a constant value of 5.5 eV when the film exceeded 30 Å thick. Photoemission results further showed that the Fermi level at the Re/HfO@sub2@ interface was partially pinned, resulting in an interface dipole of 0.5 eV and a 5.0 eV effective work function with respect with HfO@sub2@sub. C-V measurement of the Re/HfO@sub2@/SiO@subx@/n-Si stack resulted in a 4.8 eV work function of Re with respect to Si. The difference in work functions determined by photoemission and by C-V will be discussed in terms of the contribution of additional interface dipoles in the Re/HfO@sub2@/SiO@subx@/n-Si stack.

9:20am **EM2-TuM4 Oxygen Diffusion and Reduction of Interfacial Layer in high-k Metal Oxide Gate Stacks**, ***L.V. Goncharova***, Rutgers University; *M. Dalponte,* Universidade Federal do Rio Grande do Sul, Brazil; *T. Gustafsson, E. Garfunkel,* Rutgers University

Deposition of high-k metal oxide films onto Si substrates is accompanied almost unavoidably by the formation of a thin interfacial SiO@sub 2@ layer as a result of oxidation of the Si surface. This layer grows during metal oxide deposition in an oxygen-rich atmosphere or as a result of post-growth annealing treatments. Recently it has been found that deposition of an oxygen-gettering overlayer such as Ti on top of the high-k metal oxide can result in reduction and even possibly elimination of the SiO@sub 2@ interfacial layer. In our the work reported here we use Medium Energy Ion Scattering (MEIS) to focus on understanding (i) the diffusion and thermal stability of oxygen in multilayer high-k gate stacks and (ii) the reduction of interfacial SiO@sub 2@. HfO@sub 2@ films of different thickness were grown on Si(001) substrates with and without nitride incorporation on the interface. To study oxygen transport some of the films were re-oxidized in isotopically labeled @super 18@ O@sub 2@. The interfacial layer and the HfO@sub 2@ layer remain constant during deposition of the Ti overlayer at 300K, with the exception of a small amount of interdiffusion at the Ti/HfO@sub 2@ interface. There is no significant change in interfacial SiO@sub 2@. An ultra-high vacuum anneal (600K, P=10@super -9@ Torr) of the stack results in an immediate change in the oxygen region of the spectrum, accompanied by a lowering and broadening of Ti peak. This is clear evidence that some oxygen is moving towards the outer surface of the film and oxidizes Ti. The oxygen growth in the Ti layer occurs at least partially in parallel with a reduction of interfacial SiO@sub 2@ as it is suggested by a decrease of the interfacial Si peak. This process changes with increasing HfO@sub 2@ crystallinity, opening more permeable diffusive pathways via crystallite grain boundaries. Additional studies of the effects of nitrogen incorporation in the interfacial region and film thickness will be presented.

9:40am **EM2-TuM5 Characterization of High- and Low-k Dielectrics Materials using Secondary Ion Mass Spectrometry**, ***J. Bennett***, ATDF **INVITED**

The semiconductor industry continues to move forward with the introduction of high-k and low-k materials for use as gate dielectrics and interlayer insulators, respectively. The successful integration of these materials into the manufacturing process requires an understanding of the chemical, physical, and electrical properties of the new materials. Secondary ion mass spectrometry (SIMS) can provide valuable chemical information about high- and low-k materials, either using static SIMS to investigate surface chemistry or dynamic SIMS for depth profiling. However, these advanced materials are often complex mixtures of elements and physical phases that can complicate the analysis. This presentation will describe some of the current progress in the use of SIMS depth profiling to characterize both high- and low-k materials, and the challenges that remain. Examples from our lab will be used to demonstrate the difficulties (e.g., charging, beam damage) encountered when profiling new generation, porous low-k materials. Examples of backside SIMS to assess barrier metal diffusion will be also be shown. For high-k materials, particularly thin HfO@sub 2@ and HfSiO films, examples from our lab will be used to show the presence of several SIMS artifacts including preferential sputtering and sputter rate and ion variations. Also, the issue of dopant penetration through the films will be discussed.

10:20am **EM2-TuM7 Combined Electrical and Morphological Characterization of Al@sub 2@O@sub 3@ Films by Non-Contact AFM**, ***J.M. Sturm***, *A.I. Zinine, H. Wormeester, R.G. Bankras, J. Holleman, J. Schmitz, B. Poelsema,* University of Twente, The Netherlands

High-K Al@sub 2@O@sub 3@ films deposited on Si(001) by Atomic Layer Deposition (ALD) were investigated with non-contact AFM in ultra-high vacuum. Oxide charges in the film appear in the AFM images through the attractive interaction between the charge and its image charge in the conducting tip. The image contrast of the charge was found to depend on the tip-sample bias voltage. A spherical tip model based on the oxide charge, its image in the tip and the image of the tip in the substrate allows a quantitative description of the influence of the bias voltage. Most charges in the oxide film were identified as negative with a homogeneous depth distribution. Lateral variations of the Contact Potential Difference (CPD) and differential capacitance were recorded during acquisition of the topographic image with the aid of bias modulation and lock-in detection of the electrostatic force gradient at the first and second harmonic. CPD fluctuations with a typical magnitude of 20 to 50 mV on a lateral scale of ~50 nm were found. The lateral resolution of the CPD is limited with respect to the topography. This is attributed to charge screening with a length scale set by the effective Debye length. Al@sub 2@O@sub 3@ deposition on hydrogen-terminated Si (Si-H) resulted in a strong negative correlation between the differential capacitance and the surface topography (i.e. a large height correlates to low capacitance). For deposition on thermal SiO@sub 2@, this correlation was significantly reduced, whereas almost no correlation was observed for a SiO@sub 2@ film. The high correlation for deposition on Si-H is attributed to thickness variations due to substrate-inhibited ALD growth.

10:40am **EM2-TuM8 The Effect of Surface Pre-treatment upon the Growth of Hafnium Dioxide Layers on Silicon***, P. Mack, R.G. White,* ***J. Wolstenholme,*** Thermo Electron, UK*; T. Conard,* IMEC, Belgium

Angle resolved XPS (ARXPS) has been shown to be a powerful tool for the determination of the thickness of ultra-thin films. In the case of high-k dielectric layers, the technique is capable of measuring the thickness of both the high-k layer and intermediate layers of silicon dioxide or metal silicate. The values for layer thickness are in close agreement with those generated by a variety of other techniques. As well as knowing the thickness of these layers, it is important to determine whether the layers are continuous or whether the coverage of the high-k layer is only partial. Using ARXPS, a method has been developed to determine whether the coverage of the high-k material is continuous and, if not, to calculate the fraction of the surface that is covered. The method has been applied to HfO@sub 2@ layers produced using atomic layer deposition (ALD) on silicon wafers whose surfaces had received three different types of surface treatment. The way in which the layers grow and the nature of the resulting layer were found to depend upon the pre-treatment method. For example, growth on a thermal silicon dioxide surface resulted in complete coverage of HfO@sub 2@ after fewer ALD cycles than layers grown on an HF last surface. The results from ARXPS will be compared with those obtained from ToF SIMS that have been shown earlier to be a valuable alternative to the LEIS analysis.

11:00am **EM2-TuM9 Atomic Layer Deposition and Characterization of Hafnium and Aluminum Oxides and Hafnium Aluminates on Silicon***,* ***R.R. Katamreddy****, A. Deshpande,* University of Illinois at Chicago*; R. Inman, A. Soulet, G. Jursich,* American Air Liquide*; C.G. Takoudis,* University of Illinois at Chicago

In future minimization of transistor devices, alternative high dielectric constant materials are needed to replace SiO@sub 2@ and its first-generation replacement material- silicon oxy-nitride. Among the diverse number of possible candidates, HfO@sub 2@ and Al@sub 2@O@sub 3@ films are currently among the most promising replacement materials. Each of these materials has different advantageous and disadvantageous properties for the gate dielectric application. So a more optimal film may be a compositional mixture or nanolaminated structure of these two materials. In this study, the two oxide films are investigated individually on silicon in order to further investigate more complex combinations of the two metal oxides. Ultra-thin hafnium oxide and aluminum oxide films are grown on precleaned silicon substrate having approximately 10 Å residual oxide thickness. The deposition takes place in an ALD reactor using tetrakis(diethylamino)hafnium and tris(diethylamino)aluminum@footnote 1@ precursors respectively. The oxidizing co-reactant is water. After deposition, some of the resulting high-k films are annealed at 600 - 1000°C. Both deposition film and its interfacial region of annealed and non-annealed sample substrates are characterized using Fourier Transformed infrared spectroscopy, X-ray Photoelectron Spectroscopy, Scanning Transmission Electron Microscopy (STEM) and Electron Energy-Loss Spectroscopy in STEM. Our studies indicate that the as-deposited HfO@sub 2@ film is amorphous and there is no indication of silicate formation at the interface; upon annealing of these films, electron microscopy measurements reveal a novel interesting sequence of interfacial transformations as the temperature increases. Similar measurements on Al@sub 2@O@sub 3@ films will be discussed. Preliminary results on nanolaminate deposition of Al@sub 2@O@sub 3@ and HfO@sub 2@ films will also be presented. @FootnoteText@ @footnote 1@ US Patent Application Number 20050003662 A1 filed in May, 2004.

11:20am **EM2-TuM10 Measurement of Thicknesses of HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, and ZrSiO@sub 4@ Films on Silicon by Angle-Resolved XPS***, W. Smekal, W.S.M. Werner,* Vienna University of Technology, Austria*;* ***C.J. Powell,*** National Institute of Standards and Technology

We report on the use of a new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) in measuring thicknesses of candidate high-@kappa@ gate-dielectric materials (HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, and ZrSiO@sub 4@) on silicon by angle-resolved XPS. Practical effective attenuation lengths (EALs) have been computed from SESSA as a function of film thickness and photoelectron emission angle (i.e., to simulate the effects of tilting the sample). EALs have been calculated in two ways. First, realistic (Mott) cross sections have been used to describe the elastic scattering of the signal electrons in the substrate and overlayer film; appropriate inelastic mean free paths have also been selected for each material. Second, the transport approximation (TA) has been utilized in which isotropic elastic-scattering is assumed; in addition, it is assumed that elastic- and inelastic scattering parameters for the film can also be used for the substrate. These EALs have been compared with similar values obtained from the NIST Electron Effective-Attenuation-Length Database (SRD 82) that utilizes an algorithm based on the TA (and where it is again assumed that substrate and overlayer have similar scattering properties). Excellent agreement is found between EALs from SRD 82 and those from SESSA with the TA. Generally good agreement was found between these EALs and those from SESSA with the Mott cross sections, but there were some differences for film thicknesses less than the inelastic mean free path of the photoelectrons in the high-@kappa@ material. The SESSA EALs with the Mott cross sections are considered more reliable than those from the TA because realistic cross sections are used for both elastic and inelastic scattering in the film and substrate materials. These EALs should thus provide more accurate measurements of film thickness, particularly in applications where the film and substrate have different electron-scattering properties.

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