Monday Morning, November 3, 2003

High-k Gate Dielectrics and Devices Topical Conference
Room 317 - Session DI-MoM

Electronic Properties of High-k Dielectrics and their Interfaces

Moderator: R.L. Opila, University of Delaware

8:20am **DI-MoM1 Attempting the Unthinkable: Replacing SiO@sub 2@ with High-k Materials as the Gate Dielectric for Scaled Devices*, G.D. Wilk,*** ASM **INVITED**

The rapid pace of scaling CMOS technology has led to considerable attention in the area of high-k gate dielectrics. Since SiO@sub 2@ gate dielectrics are expected to have unacceptably high leakage current for most applications, high-k materials are of interest for producing lower leakage currents while maintaining similar device performance to SiO@sub 2@. Various high-k materials have been studied for this purpose recently, but it is clear that many important characteristics, which are already well known for SiO@sub 2@, have yet to be understood for any high-k material. To date, most high-k materials systems have exhibited the expected gate leakage reduction compared to SiO@sub 2@ of the same equivalent oxide thickness (EOT), but significant issues remain with respect to mobility degradation and threshold voltage shifts. Progress toward understanding these issues has been made over the past few years, yet controlling regions at both the channel and gate Si interfaces is still of critical importance to the success of any high-k material. Both physical and electrical analysis will be presented to highlight the key fundamental properties of high-k gate dielectrics, and how processing optimization has improved film quality. Characterization techniques such as electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM), medium energy ion scattering (MEIS), X-ray Photoelectron Spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) as well as electrical device properties will be presented.

9:00am **DI-MoM3 Challenges and Progress on High-K Devices and Materials*, H.-H. Tseng,*** Motorola **INVITED**

High-K gate dielectric research is critical for advanced technology because the standby power increases significantly for ultra-thin SiO2 based gate dielectric. Although progress has been made in the past, there are huge challenges remained to be solved. This paper presents the challenges and progress of High-K devices and materials. Issues related to High-K device performance such as transconductance and mobility degradation, and high threshold voltage will be discussed. Challenges of reliability related topics such as threshold voltage instability, negative bias temperature instability (NBTI), stress-induced leakage current (SILK) will also be presented. Recent progress to address these challenges will be discussed. Finally, new research directions of High-K/gate electrode stack to meet the future technology requirements will be outlined.

9:40am **DI-MoM5 First Principles Studies of the Electronic and Atomic Structures of ZrO@sub 2@/Si and ZrSiO@sub 4@/Si Interfaces*, R. Puthenkovilakam,*** *Y.-S. Lin, J.P. Chang,* University of California, Los Angeles

First principles simulations using density functional theory is employed to investigate the electronic properties of ZrO@sub 2@/Si and ZrSiO@sub 4@/Si interfaces for their potential applications in metal-oxide-semiconductor field effect transistors. Tetragonal zirconia and zircon are used to model ZrO@sub 2@ and ZrSiO@sub 4@, respectively, and the interfaces are formed by lattice matching their (001) surfaces to the Si(100) surface. The electronic structure of ZrO@sub 2@/Si interfaces showed partial occupation of zirconium d states at the Fermi level when the zirconium coordination is different from its bulk coordination. These partially occupied states lie within the silicon band gap, forming conductive paths under an applied potential field, thus are detrimental to the device performance. However, ZrSiO@sub 4@/Si interface showed no partial occupation of zirconium d states at Fermi level. Hydrogen passivation of zirconium dangling bonds as well as oxygen bridging at the interface are shown to effectively remove the partial occupancy of d orbitals. The calculated band offsets of ZrO@sub 2@/Si interfaces showed asymmetric band alignments, with conduction band offsets between 0.73-0.98 eV and valence band offsets between 3.70-3.95 eV for different zirconium and oxygen coordinations at the ZrO@sub 2@/Si interfaces. The ZrSiO@sub 4@/Si interface resulted in a more symmetric band alignment with a much higher conduction band offset of 1.90 eV and a valence band offset of 2.98 V. These results suggest that ZrSiO@sub 4@ forms a superior interface with silicon compared to ZrO@sub 2@ and can be an ideal candidate for replacing SiO@sub 2@ as a gate insulator in silicon based microelectronics and additional interface preparation or post-deposition annealing are required for ZrO@sub 2@ to yield adequate electronic properties.

10:00am **DI-MoM6 X-ray Photoelectron Spectroscopy (XPS) and Spectroscopic Ellipsometry (SE) Study of Hafnium Silicate Alloys Prepared by Remote Plasma Assisted Chemical Vapor Deposition: Comparisons between Conduction Band Offset Energies and Optical Band Gaps*, J.G. Hong,*** *N.A. Stoute, G. Lucovsky, D.E. Aspnes,* North Carolina State University

Thin films of hafnium silicate alloys, (HfO@sub 2@)@sub x@(SiO@sub 2@)@sub 1-x@, were prepared by remote plasma enhanced chemical vapor deposition (RPECVD) using down-stream injected Hf t-butoxide as the Hf source gas and silane as the Si source gas; chemically-active species from a remotely excited O@sub 2@/He plasma were used to drive the CVD reaction. Alloy compositions were determined by Rutherford backscattering (RBS), and were used to calibrate Hf-to-O spectral ratios obtained by on-line Auger electron spectroscopy (AES). XPS spectra were then obtained for the O 1s, Si 2p, Hf 4d and Hf 4f core levels, and the core level binding energies of these features were analyzed as a function of the alloy composition x. All core binding energy levels decreased (i.e., became more positive) as the Hf fraction x increased, paralleling the behaviors previously reported for O 1s, Si 3p, and Zr 3d core level energy shifts in zirconium silicate alloys. The Hf silicate alloy shifts are consistent with the charge transfer expected on the basis of the relative electronegativities of Hf, Si and O. As in case of Zr silicates, the total shift of the O 1s core level in Hf silicates, ~3.1 eV, is larger than the average shift of the Hf 4d and Si 2p core levels, ~ 2 eV. Finally, the XPS results will be compared with on-line AES, X-ray absorption spectroscopy (XAS), and vacuum ultra-violet spectroscopic ellipsometry (SE) results to determine the compositional variations of the conduction and valence band offset energies with respect to Si, and to compare theses with the compositional variation of the optical band gap.

10:20am **DI-MoM7 Photoemission Study of High-k Gate Dielectric/Si(100) Heterostructures - Chemical Bonding Features and Energy Band Alignment*, S. Miyazaki,*** Hiroshima University, Japan **INVITED**

The characterization of chemical and electronic structures of high-k dielectrics as well as the quantification of defect state distributions is of great importance for the implementation of the high-k dielectric gate stack in sub-100nm technology generations. For some high-k dielectrics such as Ta@sub 2@O@sub 5@, Al@sub 2@O@sub 3@, ZrO@sub 2@ and HfO@sub 2@, we have experimentally determined the energy band alignments to Si(100) with an thin interfacial Si-oxide or nitride from high-resolution XPS measurements and defect state distributions in the high-k dielectrics and at the interfaces form total photoelectron yield measurements.@footnote 1-3@ We have extended our research to characterize the chemical and electronic structures of Y@sub 2@O@sub 3@, Pr-silicates and Hf-aluminates on Si(100) including interfacial SiO@sub x@. In this presentation, recent our results will be review to demonstrate how the energy bandgaps of practically-thin high-k dielectrics such as HfO@sub 2@ and Y@sub 2@O@sub 3@ and of an ultrathin Si-nitride barrier can be determined from the analysis of energy loss spectra of O1s (or N1s) photoelectrons and, for the system of Y@sub 2@O@sub 3@ formed on Si(100), how the energy band alignment can be determined with combination of the measured bandgap and the valence band lineup as obtained from the analysis of XPS valence band spectra of heterostructures with thin dielectrics. Also, we show that total photoelectron yield spectroscopy is a useful tool for quantifying the energy distribution of electronic defect states for thin high-k dielectric/Si(100) systems. @FootnoteText@@footnote 1@S. Miyazaki, J. Va. Sci. Technol. B19, (2001) 2212. @footnote 2@S. Miyazaki, M. Narasaki, M. Ogasawara and M. Hirose, Microelec. Eng., 59 (2001) 373. @footnote 3@M. Yamaoka, M. Narasaki, H. Murakami and S. Miyazaki, Proc. of 2nd Int. Semicond. Technol. Conf. (2002, Tokyo) Abst. No. 57.

11:00am **DI-MoM9 Separate and Independent Control of Interfacial Band Alignments and Dielectric Constants in Transition Metal-rare Earth Ternary Oxides*, D.G. Schlom,*** Pennsylvania State University*; J.L. Freeouf,* Oregon Graduate Institute*; G. Lucovsky,* North Carolina State University

The electronic structure of transition metal, Tm, and trivalent rare earth, Re, binary (TmO@sub x@ and Re@sub 2@O@sub 3@) and ternary mixed oxides (TmRe@sub x@O@sub y@) are qualitatively different from those of silicon oxide, silicon nitride, and silicon oxynitride alloys. The lowest conduction band states are associated with localized anti-bonding d*-states of the Tm/Re atoms, rather than extended Si 3s*-states, and/or O/N 2p*-states. Based on quantitative agreement between the Zr silicate anti-

bonding state electronic structure obtained from Zr M@sub 2,3@ and O K@sub 1@ XAS spectra, and ab initio calculations on small clusters, the ordering and overlap of anti-bonding Zr 4d*- and 5s*-states, and Si 3s*-states in the O K@sub 1@ spectra is the same as the features of the conduction band electronic structure that determine band-offset energies at Si-Zr silicate alloy interfaces. These relationships have been extended to Re ternary oxide compounds, including LaAlO@sub 3@ and GdScO@sub 3@, through direct comparisons between O K@sub 1@ XAS spectra and band edge optical absorption constants obtained from analysis of SE measurements extending to 9 eV. As a result of near-neighbor interactions between Tm and Re d-states induced by bonding to a common O atom, ternary oxide minimum band gaps, and conduction band offset energies are increased in oxide phases containing Tm and Re species. This identifies new and technologically important opportunities for band gap engineering at the atomic scale. Relative energy shifts of coupled Re and Tm d*-states are important for the ultimate scaling of CMOS devices since they increase the effective band gaps/offset energies for ternary oxides containing highly polarizable Sc, Ti, Nb, and Ta atoms above what had previously been proposed as a fundamental limitation inferred from the band gaps and/or band offset energies of their respective binary oxides.

11:20am **DI-MoM10 A Materials and Electronics Properties Study of the ZrO@sub 2@/Si and SiO@sub 2@ Interfaces***, **C.M. Lopez**, N.A. Suvorova,* University of North Carolina, Chapel Hill*; A.A. Suvorova, M. Saunders,* University of Western Australia*; E.A. Irene,* University of North Carolina, Chapel Hill

Zirconia, ZrO@sub 2@, thin films were grown on single crystal MgO(100), Si(100) and on amorphous SiO@sub 2@ by ion beam sputter deposition of Zr metal at room temperature and subsequent oxidation both in-situ and ex-situ at 250°C and 600°C, respectively. The optical properties of MgO, sputter-deposited Zr, and ZrO@sub 2@ were determined by in-situ spectroscopic ellipsometry in the photon energy range of 1.5-4.5 eV. Based upon ellipsometric thicknesses obtained, a volume expansion of 1.28 Zr to ZrO@sub 2@ was observed. This value is in contrast to the value assuming bulk densities, 1.54. Refractive index values for ZrO@sub 2@ ranged from 2.18 to 2.52 for the given spectral range. Time of flight mass spectrometry of recoiled ions (TOF-MSRI), analytical electron microscopy, and spectroscopic ellipsometry were used to investigate the material properties of all samples with special attention to the composition and extent of the interface formed between ZrO@sub 2@ and the Si substrate. To compliment these techniques, electrical measurements were performed on fabricated Pt/ZrO@sub 2@/Si capacitors also prepared in vacuo to determine the interface trap state density, fixed charge, and dielectric constant for the overall film stack. The nature of the interface is correlated with the resultant electronic properties of the interface.

11:40am **DI-MoM11 Interface and Materials Properties of High-k Gate Stack Structures***, **S. Sayan**, X. Zhao, R.A. Bartynski, T. Emge, M. Croft, T. Gustafsson, D. Vanderbilt, E.L. Garfunkel,* Rutgers University

In this presentation, we describe recent results using soft x-ray photoemission (SXPS), inverse photoemission (IPE), and x-ray absorption spectroscopy (XAS) to examine HfO2 gate dielectrics and their interfaces with silicon and metal layers. In selecting an alternative (high-K) gate insulator, many parameters in addition to dielectric constant and thermal stability must be considered, including the barrier heights for tunneling. The SXPS and IPES results are used to determine the densities of states above and below the Fermi energy, in particular to elicit useful information on barrier heights. We find that interface dipoles affect the "effective workfunction" of metals via change in electrostatic potential as well as the band alignments, where the specific alignment depends on the interface properties. We have also performed first-principles density functional calculations to study the properties of the crystalline phases of HfO2 and ZrO2. The densities of valence and conduction bands are calculated and compared to experimental measurements. The thickness, layered structure, and crystal phase of the as-deposited and annealed films have been studied by XRD, XAS, MEIS, RBS and HRTEM. The authors would like to acknowledge useful interactions with colleagues at and NCSU (J.P. Maria, G. Parsons, G. Lucovsky and A. Kingon), J.Robertson (Cambridge University.UK), R. Tung (CUNY) and K.P. Cheung (ECE, Rutgers University) We also acknowledge the SRC for financial support.

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