

Electronic Materials and Processing Room 304B - Session DI-MoA

High-k Dielectrics: Electronic Properties

Moderator: T. Klein, The University of Alabama

2:00pm **DI-MoA1 Metal Nitride Gate Electrode Effects on Dielectric Properties of HfO₂ and Hf-doped TaO_x High-k Gate Dielectrics**, *Y. Kuo, J.-Y. Tewg, J. Lu*, Texas A&M University; *P. Majhi, G. Bersuker*, Sematech

High-k gate dielectrics with appropriate gate electrodes are critical to future MOS device performance. Metal oxides, such as hafnium oxide and various doped tantalum oxides, are promising high-k materials. Since polysilicon has many practical limits for the high-k gate electrode application, e.g., undesired interface layer formation and dopant diffusion, other conductive materials are being actively sought for this purpose. Metal nitrides are possible candidates because they can be easily prepared by the sputtering method, are usually difficult to react with the adjacent oxide, and are good diffusion barriers. In this paper, authors investigated the influence of various types of metal nitride electrodes, i.e., molybdenum nitride MoN, tungsten nitride WN, and tantalum nitride TaN, on electrical characteristics of MOS capacitors composed of a high-k dielectric layer of hafnium oxide or Hf-doped tantalum oxide. Hafnium oxide was deposited by atomic layer deposition ALD and the doped tantalum oxide was deposited by reactive sputtering. Dielectric properties, such as EOT, leakage current, flatband voltage, metal work function, and interface state density, were studied. Process parameters, such as the annealing temperature and atmosphere were varied for their influence on the electrical properties. The interface and bulk film material properties were characterized with ESCA, XRD, and TEM. Dielectric properties were dramatically influenced by the nitride electrode and the process parameters. We are going to discuss the cause of the difference with respect to material and interface layer changes during the process.

2:20pm **DI-MoA2 d-states Coupling in Mixed High-k Oxides: Transition Metal Oxide Binary Alloys, and Transition Metal-rare Earth Complex Oxides**, *G. Lucovsky, C.C. Fulton, Y. Zhang, J.L. Whitten, R.J. Nemanich, H. Ade*, NC State University; *D.G. Schlom*, Penn State University; *J.L. Freeouf*, Oregon Research Institute; *Y. Zou*, NC State University

The lowest conduction band anti-bonding d*-states in (HfO@sub 2@)@sub x@(TiO@sub 2@)@sub 1-x@ pseudo-binary alloys, and in TiO@sub 2@ and HfO@sub 2@ have been studied by soft x-ray absorption spectroscopy (XAS). These studies distinguish between intra-atomic transitions within the Ti- and Hf-atoms and inter-atomic transitions that involve mixing of the Ti and Hf d*- and s*-states with O 2p*-states. Comparisons between the energies of the lowest d*-states in the O K@sub 1@ spectra of TiO@sub 2@ and HfO@sub 2@ indicate that the energy difference between these features is essentially the same as the energy difference between d*-state features at the respective band edges. There are systematic changes in the d*-state features of the alloys that are consistent with the coupling of valence band d-states of Ti- and Hf-atoms through bonding a common O-atom. This mixing has confirmed through complementary changes in the valence band electronic structure as deduced from ultra-violet photoelectron spectroscopy (UPS). Ab initio quantum chemistry molecular orbital calculations indicate that d-state coupling is maximized when the respective d-states of the Ti- and Hf-atoms have the same symmetry, and the Ti-O-Hf bonding group is collinear. This results in two coupled modes. The O K@sub 1@ edge spectrum of a HfTiO@sub 4@ film (x = 0.5), crystallized by annealing at 800°C, shows three d*-features, indicating that the coupling of Hf 5d*- and Ti 3d*-states is not optimized. Non-optimized coupling of d*-states associated with a dynamic Jahn-Teller effect has also been found in the complex lanthanide rare earth/transition metal oxides, Gd(Dy)ScO@sub 3@. Non-optimized d-state coupling is also evident in band edge spectra. The relationships between d-state coupling and band gap engineering of high-k dielectrics will be discussed.

2:40pm **DI-MoA3 Theoretical Analysis of High-K Dielectric Interfaces with Silicon and Metals**, *A.A. Demkov*, Motorola, Inc. **INVITED**

The scaling of the complimentary metal oxide semiconductor (CMOS) technology requires the replacement of silicon dioxide with a high dielectric constant (high-k) material as a gate dielectric. Having a high-k film in the gate stack results in a capacitance equivalent to a much thinner film of a dielectric with a lower dielectric constant. The benefits of a high-k material are thus twofold, a higher capacitance results in a higher saturation current and improves the performance, and the increased

thickness cuts down the gate leakage current and improves the power consumption. Successful implementation of a high-k dielectric in CMOS depends upon our ability to control the interfacial properties. The chemistry at the Si/dielectric and dielectric/electrode interfaces is determined by atomic-scale interactions, which ultimately sum to yield the electrical properties such as the threshold voltage observed macroscopically. A rigorous attempt to predict and control the interface behavior, therefore, must be based on the atomic-scale characterization and first-principle calculations. In this talk I will review the recent theoretical work on the interfaces of high-k dielectrics with Si and metals, and in particular, the calculations of the band alignment at the interface. I will discuss relative advantages of amorphous vs crystalline oxides (including epitaxial oxides). A connection will be made to the device characteristics such as the threshold voltage by means of using the results of density functional calculations in TCAD simulations.

3:20pm **DI-MoA5 Nitrided Hafnium Silicates for Gate Dielectrics**, *C.-G. Wang, H. Velasco, M. Verghese, E. Shero, G. Wilk*, ASM America Inc.; *J.W. Maes, O. Laitinen*, ASM International, Belgium; *W. Deweerd, A. Delabie*, IMEC, Belgium; *R.L. Opila, A. Mathew, K. Demirkan*, University of Delaware; *J. Morais, I.J.R. Baumvol*, Universidade Federal do Rio Grande do Sol, Brazil
Nitrided hafnium silicate (HfSiON) gate dielectric films deposited by atomic layer chemical vapor deposition (ALCVD@super TM@) show excellent capacitor and transistor characteristics with both poly-Si and metal gates, which are directly correlated with local physical and chemical properties. A wide range of compositions are demonstrated, with Si/(Hf+Si) percentages from 0 to 75% and uniformly distributed N levels up to 30 at. %. XPS is used to distinguish the local bonding arrangements of N to Hf, Si and O. The distribution and depth profile of these N bonds is directly attributable to the observed electrical and physical properties of these films as measured by TOF-SIMS, TEM, EELS, nuclear reaction analysis and angle-resolved XPS. Using poly-silicon gate electrodes with chemical or thermal oxide underlayers, EOT values down to 1.3 nm with substantial leakage reduction vs. SiO@sub 2@ have been achieved using stacks with ultrathin HfSiON. Hysteresis and midgap interface density (D@sub it@) are less than 10 mV and 5X10@super 10@ cm@super -2@eV@super -1@, respectively. Transistors (gate length of 110nm) with these ALD HfSiON films display excellent V@sub T@ stability and channel electron mobility > 90% of SiO@sub 2@ at high E@sub eff@. Detailed analysis on silicate compositions, the distribution of nitrogen in the interface layers, and corresponding impact on device performance will be presented.

3:40pm **DI-MoA6 Optical Properties of Prospective High-k Dielectric Films**, *E. Cicerella, J.L. Freeouf*, OGI School of Science & Engineering of OHSU; *L.F. Edge, D.G. Schlom*, The Pennsylvania State University; *T. Heeg, J. Schubert*, Inst. fur Schicht und Ionentech., Germany; *S.A. Chambers*, Pacific Northwest National Laboratory

The current gate dielectrics in silicon MOSFETs are unable to prevent excessive gate leakage as devices continue to shrink. The effort continues to establish appropriate materials to replace SiO₂ to remove this problem. New processing issues arise as we deal with these new materials especially as they are deposited on Si substrates. We have established that some rare earth perovskites have high dielectric constants. We believe that they will be thermodynamically stable with silicon and therefore are possible gate dielectrics. We discuss thin films of one candidate material, LaScO₃, which were grown by molecular beam deposition on Si substrates and pulsed laser deposition on MgO substrates. Using spectroscopic ellipsometry in the Far UV (5 eV - 9 eV) and the UV/VIS (1.5 eV - 5 eV), as well as transmission studies between 1.5 eV and 6 eV, we have established that low temperature deposition leads to a reduced band gap and a lower density as compared with the bulk crystal. We seek to understand the impact of deposition technologies as well as other process steps, such as high temperature anneals. To this end we have had high temperature anneals performed on these films and then repeated these measurements and analysis. In this analysis we shall seek changes in density, band gap, refractive index, and interfacial layers between the substrate and the deposited film.

4:00pm **DI-MoA7 Spectroscopic Studies of Valence Band States in HfO₂, TiO₂, ZrO₂ and HfTiO₄ by Soft X-Ray and Vacuum Ultra-Violet Photoemission Spectroscopy**, *C.C. Fulton, G. Lucovsky*, North Carolina State University

Valence bands of HfO@sub 2@, TiO@sub 2@, ZrO@sub 2@ and HfTiO@sub 4@ films have been studied by soft x-ray photoemission spectroscopy (SXPS) at energies between 70 and 170 eV, and by He I and II ultra-violet photoemission spectroscopy (UPS) at energies of 21.2 and 40.8

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eV. For HfO₂, SXPS studies reveal two valence bands as well as the Hf 4f doublet, whereas He I UPS studies have probed only the uppermost valence band. SXPS and UPS energies are referred to an extrapolated threshold energy at 8.1±0.2 below vacuum, or ~3 eV below the valence band edge of c-Si. The first SXPS valence band has features at 2.2±0.2 eV and 6.2±0.2 eV. The 4f doublet components are at 13.7±0.2 eV and 15.4±0.2 eV. The second valence band is centered at ~22 eV. The UPS valence band displays features at 1.5±0.2 eV and 5.2±0.2 eV. Energies of the symmetry determined valence band molecular orbitals have been obtained from ab initio calculations on relatively small clusters. The top of the valence band is assigned to O 2p π non-bonding states. With this as a reference, calculated MOs are: Hf 5d π + O 2p π at 0.5±0.2 eV and Hf 5d σ + O 2p σ at 5.4±0.2 eV, with an energy difference of 4.9±0.3 eV, and O 2s at 22.2±0.2 eV. Setting the valence band edge to the O 2p π non-bonding energy, and averaging SXPS and UPS spectra, the experimental MOs in the first valence band are at 1.8±0.2 eV for Hf 5d π + O 2p π, and 5.7± eV for Hf 5d σ + O 2p σ, with an energy difference of 3.9±0.3 eV. The O 2p π non-bonding and Hf 5d π + O 2p π bands overlap and contribute to a broad spectral feature, and this resulting agreement between theory and experiment is good. The average energy of the O 2s band is 22±0.3 eV, and is in excellent agreement with the calculated energy of 22.2 eV. The paper will also include SXPS and UPS valence band studies for TiO₂, ZrO₂ and HfTiO₄.

4:20pm DI-MoA8 Electronic Properties and Band Alignments of Hf-based Gate Dielectrics on Silicon, R. Puthenkovilakam, J.P. Chang, University of California, Los Angeles

Ultra thin HfO₂ or HfO_xN_y thin films are being considered for possibly replacing SiO₂ gate oxide in silicon based metal-oxide-semiconductor (MOS) transistors. In this work we investigated the electronic structure and band alignments at the HfO₂/(or HfO_xN_y)/Si interfaces which dictate the device performance of transistors in the sub-90nm devices. We used tetragonal structure to model HfO₂ and nitrogen incorporation was achieved by replacing selective oxygen atoms with nitrogen. The electronic structure of HfO₂/Si interface showed dangling bond states at the interface due to the reduced coordination of Hf caused by the intrinsic bond constraints at the HfO₂/Si interface. However, our calculations indicate that these dangling bonds could be passivated by hydrogen or oxygen, which can appropriately change the coordination numbers at the interface, thereby removing the dangling bond states. We also considered the interface of HfSiO₄/Si and found that there are no dangling bond states at this particular interface, making HfSiO₄ a promising interfacial layer to improve the interface quality. Band offsets at the HfO₂/Si interfaces were theoretically calculated and showed that the conduction band offsets ranged from 1.5-1.9 eV depending upon the interface stoichiometry. Band offsets were experimentally determined by measuring the core level to valence band maximum binding energy differences using XPS and were in excellent agreement with the theoretical results. Incorporation of nitrogen into the HfO₂ network resulted in notable changes in the valence band structure of the material and the corresponding band alignments with silicon and is found to depend on the nitrogen concentration in the bulk of HfO₂ as well as at the interface.

4:40pm DI-MoA9 Interface Band Alignment in High-k Gate Stacks, P. Hartlieb, E. Bersch, Rutgers University; S. Sayan, National Institute of Standards and Technology; R. Bartynski, E. Garfunkel, Rutgers University

Understanding and controlling band alignment remains a key aspect that must be realized if novel materials are to be incorporated in future nano-electronic devices. Photoemission, inverse photoemission, internal photoemission, and complementary methods have been used to examine (i) amorphous high-K gate dielectrics and their interface on Si, (ii) metal-oxide interfaces, and (iii) multilayered gate stacks that include metal gates and high-K dielectrics. Materials changes occur at the various interfaces during growth and processing that strongly effect device properties including the band alignment. The potential changes (effective work function) across the films have been examined as a function of material, thickness and processing ambient. Experimental results are compared to theoretical calculations to better understand the electronic properties of the different crystalline structures. It is found that the band gap, barrier height and dielectric response of this class of materials are very phase-dependent. Inverse photoemission measurements show that the conduction band shifts to higher energy going from HfO₂ to HfSiO with increasing SiO content. In contrast, addition of nitrogen shifts the

conduction band to lower energy. The conduction band edge of HfO₂ rapidly shifts to lower energy upon Al metallization @footnote 1@. @FootnoteText@ @footnote 1@ The SRC, iSematech, and NSF are gratefully acknowledged for their financial support.

5:00pm DI-MoA10 A New Approach to the Synthesis of Zr Oxynitride Alloys: Chemical and Electrical Characterizations, B. Ju, G. Lucovsky, NC State University

In order to suppress chemical phase separation in Zr silicate alloys, (ZrO₂)_x(SiO₂)_{1-x}, at temperatures up to 900°C, N-atoms have been incorporated into these alloy films by a remote plasma assisted process. Our studies indicated that N-atoms were not incorporated uniformly by this plasma process. This paper provides an alternative synthesis route that produces uniform N-atom incorporation, and also prevents formation of O-N bonds that are observed in the plasma modified Zr silicate films. In this study, Zr-Si oxynitride [(ZrO₂)_x(SiO₂)₃N₄)_y(SiO₂)_z], x+y+z = 1, pseudo-ternary alloy films have deposited on Si (100) wafers by low temperature (300°C) remote plasma enhanced chemical vapor deposition (RPECVD). Film compositions were determined by Rutherford back scattering (RBS) and these were used to calibrate on-line Auger electron spectroscopy (AES). In general, the ZrO₂ concentration could be held relatively constant for SiO₂ rich alloys, y < z, but decreased in the Si₃N₄ rich alloy regime in which y > z. The local bonding of Zr-, Si-, O- and N-atoms in as-deposited, and annealed Zr-Si oxynitride alloys were investigated by x-ray photoemission spectroscopy (XPS) as a function of alloy composition. Previous studies have indicated that changes in the O-atom 1s core level feature provided a way to detect chemical phase separation. In alloys with up to 20 % ZrO₂ fraction, no chemical phase separation or compositional changes were detected after rapid thermal annealing (RTA) up to 1100°C in Ar for 1 minute. Capacitance-voltage (C-V) and leakage-voltage (J-V) studies were performed on metal-oxide-semiconductor (MOS) capacitors fabricated on both n-type and p-type Si substrates, and these results will be presented in the paper.

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