Friday Morning, November 17, 2006

Electronic Materials and Processing
Room 2003 - Session EM+TF-FrM

High-k Dielectric & Multi-Functional Oxide Growth & Processing

Moderator: R.L. Opila, University of Delaware

8:00am **EM+TF-FrM1 Chemical Analyses and Electrical Studies of HfO@sub 2@/Y@sub 2@O@sub 3@, Y@sub 2@O@sub 3@/HFO@sub 2@ Bilayered and Y@sub x@Hf@sub y@O@sub z@ Intermixed Dielectric Materials for MIM Capacitors***, M. Kahn, C. Vallee, C. Dubourdieu, M. Bonvalot, J.R. Plaussu, J. Ducote, T. Baron, O. Joubert,* LTM/CNRS, France

Improving the capacitance density of MIM devices constitutes a real challenge to satisfy scaling rules for next IC generations and to reduce the cost as well. Silicon dioxide and nitride have been commonly used up to date as dielectrics in conventional MIM capacitors. However, they cannot provide capacitance values larger than 2fF/µm@super 2@. With further scaling going on at an active pace, high-@kappa@ dielectric materials offer a viable alternative to provide both high capacitance density and low leakage currents. This dielectric material of a MIM device has to meet several requirements such as a high capacitance density, low leakage currents and minimum variation of capacitance values with voltage bias. In a previous work, we studied TiN/Y@sub 2@O@sub 3@/Au capacitors and showed that Y@sub 2@O@sub 3@ exhibits appropriate electrical properties with low leakage currents and a capacitance density of 5 fF/µm@super 2@ @foonote 1@. However, we observed that the capacitance density cannot be further increased without a substantial increase in the leakage current, which in turn exceeds ITRS requirements. The aim of the present work is to overpass this capacitance limitation thanks to the introduction of a bilaminate dielectric material. Studies of MIM capacitors based on HfO@sub 2@/Y@sub 2@O@sub 3@, Y@sub 2@O@sub 3@/HFO@sub 2@ bilaminate and intermixed Y@sub x@Hf@sub y@O@sub z@ dielectric materials will be presented. These high @kappa@ dielectric layers are prepared by pulsed injection MOCVD on WSi@sub x@ bottom electrodes and the gold top electrode is realized by evaporation. The electrical behavior C(V) and I(V) of the obtained structures will be presented and discussed in terms of capacitance density, capacitance linearity and leakage currents. They will be correlated to chemical analysis results (XPS and SIMS), with special attention devoted to metal/oxide and oxide/oxide interface investigations. In particular, the observation of a non symmetrical C(V) curve will be highlighted with respect to the bilaminate stack HfO@sub 2@/Y@sub 2@O@sub 3@ and Y@sub 2@O@sub 3@/HFO@sub 2@ of dielectric materials. @FootnoteText@ @footnote1@ C. Durand, C. Vallee, C. Dubourdieu, M. Kahn, M. Derivaz, S. Blonkowski, D. Jalabert, P. Holliger, Q. Fang, I.W. Boyd ; J. Vac. Sci. Technol to be published (May/June 2006).

8:20am **EM+TF-FrM2 Process-Dependent Interface States at Mo/Hafnium Oxide/Si Interfaces***, **S. Walsh**, L. Fang,* The Ohio State University*; J.K. Schaeffer, E. Weisbrod,* Freescale Semiconductor, Inc.*; L.J. Brillson,* The Ohio State University

A major challenge for Hafnium Oxide (HFO) and other high-K dielectric materials is the control of their interface state and trapped charge densities. Among the chief electronic and chemical requirements for their development is the identification of post-growth processes to optimize oxide bonding within the thin dielectric films and at their interfaces. This requires characterization techniques that are nondestructive, that can measure electrically-active defects that correlate with electrical device features, and that can spatially isolate these defects within ultra-thin films to help identify their physical origins. We have used low energy electron-excited nanoscale-depth-resolved (DRCLS) spectroscopy to probe the bulk and interface defect states of ultra-thin Mo/HFO/Si with 8 different process sequences. After atomic layer deposition (ALD) of 4 nm HfO@sub 2@ on Si and an O@sub 2@ post treatment, we deposited 10 nm Mo using either plasma vapor or electron beam deposition, with or without a subsequent 1000@super O@C N@sub 2@ anneal, and with or without a forming gas anneal. DRCLS revealed pronounced gap state emissions within the ultrathin films and their interfaces with Mo and Si. There are multiple deep level emissions below the 5.5 eV band gap, including 3 peak emissions at 3.4, 3.5 eV, and 3.9-4.3 eV that can be associated with HFO oxygen vacancies in different charge states predicted theoretically.[1] In addition, states at 2 -2.6 eV that resemble known SiO@sub 2@-related nonbonding oxygen hole centers (NBOHC) and E' (positively charged O vacancy) native defects increase with depth within the 4 nm HFO film suggesting the formation of a Hf silicate at the HFO/Si interface. Furthermore, different process steps produce large changes in these states and for at least one sequence, a dramatic decrease in both types of defects. The differences between process sequences can be understood in terms of known reactions at HFO-Si interfaces.

8:40am **EM+TF-FrM3 Materials Challenges for High Permittivity Gate Dielectrics and Metal Gate Electrodes***, **J.K. Schaeffer**, D. Gilmer, S. Samavedam, M. Raymond, D.H. Triyoso, R.I. Hegde, M. Stoker, S. Kalpat, C. Capasso, B. Taylor, P.J. Tobin, B.E. White,* Freescale Semiconductor, Inc.*; S. Walsh, L. Fang, L.J. Brillson,* The Ohio State University **INVITED**

This talk will review recent advances and remaining challenges associated with high-k gate dielectrics and metal gate electrodes with a specific focus on the fundamental materials properties responsible for critical device characteristics. Recent reports have shown that alloying ZrO@sub 2@ into HfO@sub 2@ improves device reliability and effective oxide thickness (EOT) scaling. This talk will review the structural and electrical properties of Hf@sub x@Zr@sub 1-x@O@sub 2@ films that impact EOT and device reliability. Next, to better understand the nature of the metal/HfO@sub 2@ interface, the previously established empirical relationship between the mean electronegativity and effective work function developed for Schottky contacts has been applied to multi-element electrode materials on hafnium dioxide gate dielectrics. Our data show good agreement with the pre-existing framework established for metal/insulator contacts, and illustrates the important role that sub-lattice elements such as N and C can have on effective work-function. This understanding helped lead to the development of tantalum carbide as a thermally stable NMOS gate electrode candidate. Finally, many device properties result from the electrical and chemical interactions between the various gate stack layers which can lead to differences in EOT growth, increased dielectric leakage, fixed charge, and changes in effective work function. The selection of the gate metal can have a pronounced impact on these properties. Such interactions are likely responsible for the difficulty in manufacturing devices with low PMOS device threshold voltages and scaled EOT on silicon substrates. Recent experiments are now providing new insights into the origins of this problem.

9:20am **EM+TF-FrM5 Molecular Beam Epitaxy of Multifunctional Materials Using a Chloride Refractory Metal Chemistry***, **W.A. Doolittle**, A.G. Carver, W. Henderson, W. Laws Calley, S.-S. Kim,* Georgia Institute of Technology **INVITED**

Multifunctional materials, materials that interact with their environment via differing force mechanisms, including but not limited to electrostatic, magnetic, acoustic, photonic, and chemical, are of great interest for future sensor and actuator applications. Lithium metal oxide multifunctional materials, including LiNbO@sub 2@, LiNbO@sub 3@, LiTaO@sub 2@ and LiTaO@sub 3@ are presented as a promising but challenging materials for multifunctional devices. Example proposed applications will be presented. A chloride based chemistry that bypasses many of the traditional pitfalls of Lithium Niobate (LN) epitaxy including the need for electron beam evaporation of refractory metals, and use of complex metal organic precursors prone to pre-reaction is described. Methods of dealing with the normally corrosive chloride based chemistry in a Molecular Beam Epitaxy (MBE) chamber are detailed. The present state of homoepitaxy and heteroepitaxy of LN on semiconductors is presented. It is shown that LiNbO@sub 2@ is preferentially grown over LiNbO@sub 3@ in the oxygen deficient MBE vacuum environment. However, LiNbO@sub 2@ is shown to be converted to LiNbO@sub 3@ by an ex-situ oxygen anneal. Dramatic changes in optical properties and crystalline lattice structure result and will be detailed. A limited stoichiometry control is demonstrated via use of ion filters on an oxygen plasma source including the ability to partially select between various valences of niobium oxides, NbO, NbO@sub 2@ and Nb@sub 2@O@sub 5@. While the demonstrated metal chloride based epitaxy is shown as a viable candidate for MBE of multifunctional refractory metal oxides, particularly for electronic applications, the possibility for thicker films, and thus impact on optical devices, is currently limited by the available Li source. Efforts to circumvent this difficulty, including a large volume valved Li source, will be described.

10:00am **EM+TF-FrM7 Magnesium Oxide Thin Film 'Bridge' on Hexagonal Silicon Carbide for Integration of Functional Oxides***, T.L. Goodrich, Z. Cai,* ***K.S. Ziemer**,* Northeastern University

Single crystalline MgO (111) films, 15 to 100 Å thick, have been grown on hexagonal silicon carbide (6H-SiC) in order to integrate complex oxides, such as lead zirconate titanate [PZT], with SiC high-power, high-

temperature, high-frequency devices with multiple functionalities. 6H-SiC substrates (0001)@sub Si@ and (000I)@sub C@ were cleaned to create atomic steps hundreds of nanometers wide and 1.5 nm high, and reduce oxygen contamination from 12% to 8% for the (0001)@sub Si@ surface and from 8% to 3% for the (000I)@sub C@ surface, as measured by x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy. The residual oxygen concentration was determined by reflection high energy electron diffraction (RHEED) to be incorporated into a @sr@3x@sr@3 R30° silicate adlayer reconstruction. MgO films were grown using a remote oxygen plasma source to produce a constant chamber oxygen pressure (5x10@super -6@ Torr) and a solid source Mg effusion cell at various Mg fluxes but constant Mg fluence. The (000I)@sub C@ surface and the (0001)@sub Si@ surface of the SiC produce differently structured films, as measured by RHEED and atomic force microscopy (AFM), under the same molecular beam epitaxy growth conditions. All films are roughly stoichiometric as measured by XPS, with some suggestions of Mg metallic bonding near the substrate. MgO thin films grown on (0001)@sub Si@ oriented SiC substrates were three-dimensional and crystalline at low Mg flux but became more conformal and improved single crystalline as the Mg flux was increased. The opposite was observed for (000I)@sub C@ oriented SiC. At Mg fluxes than 1x10@super 14@ atoms/cm@super 2@s, the films were conformal but highly polycrystalline. As the Mg flux was increased, the crystalline MgO thin films became less polycrystalline but exhibited more 3-D morphology. Current studies will compare the deposition of BaTiO and PZT on the MgO thin films to those deposited directly on the cleaned SiC substrates.

10:20am **EM+TF-FrM8 Zirconium Dioxide Formation on Silicon Surfaces by Metal-Organic Chemical Vapor Deposition in UHV**, ***A. Sandell**, P.G. Karlsson, J.H. Richter,* Uppsala University, Sweden*; J. Blomquist, P. Uvdal,* Lund University, Sweden*; T.M. Grehk,* Hogskolan Dalarna, Sweden

Previous work has shown that deposition of zirconium tetra-tert-butoxide at elevated temperatures leads to the formation of a ZrO2 film. The previous studies also reveal the presence of an interfacial region between the Si substrate and the ZrO2 film. However, up to date, the evolution of the interface has not been comprehensively addressed using surface science techniques. In this contribution, a detailed study of the growth and interface formation on Si(100) and Si(111) in UHV is presented. Core level photoelectron spectra provide information on the growth rate, atomic oxidation state and the chemical composition of the interface, including the fate of the butoxy ligands. X-ray absorption spectra give valuable complementary information on the local geometric structure of the Zr-O units and the Zr-O electronic interaction. In addition, STM images of the first stages of nucleation are shown. These suggest that it is possible to distinguish between precursors induced defects on the Si(100) surface related to oxidation and reaction with carbonaceous fragments, respectively.

10:40am **EM+TF-FrM9 Controlling Interfacial Reactions between HfO@sub 2@and Si using Ultra-Thin Diffusion Barriers**, ***R.R. Katamreddy,*** University of Illinois at Chicago*; R. Inman, G. Jursich, A. Soulet,* American Air Liquide*; C.G. Takoudis,* University of Illinois at Chicago

Hafnium oxide has gained considerable interest in recent years as a potential high-k dielectric material for future fabrication of complementary metal oxide semiconductor devices. One of the problems with HfO@sub 2@ is its interfacial reactivity with Si at the high temperature necessary for post deposition annealing. Our previous studies have shown that HfO@sub 2@ films on Si form silicates and silicides at the interface as low as 600 °C and this is not suitable for CMOS process integration. In this study we examine the effectiveness of ultra-thin Al@sub 2@O@sub 3@ as a HfO@sub 2@-Si diffusion barrier up to 1000 °C. Al@sub 2@O@sub 3@ has superior interface stability with Si but it also has a lower dielectric constant than HfO@sub 2@. So, to minimize reduction in overall dielectric constant of the film with this barrier layer, there is a need to understand how thin the Al@sub 2@O@sub 3@ layer can be in this system and yet still maintain its effectiveness as a barrier. Our studies have shown 0.5 nm of alumina was sufficient to prevent formation of silicates and silicides of hafnium at temperatures below 1000 °C, while thicker alumina films were required to prevent the same at 1000 °C. The ultra-thin dual layer films are prepared by sequential atomic layer deposition of Al@sub 2@O@sub 3@ and HfO@sub 2@ using tetrakis(diethylamino)hafnium and tris(diethylamino)alane as the metal oxide precursors and water vapor as the oxidizer. Nitrides and oxynitrides of silicon are some other promising diffusion barriers. Silicon nitride and oxynitride are also investigated as potential barrier layers for HfO@sub 2@-Si. After deposition, the films are subjected to high temperature annealing up to 1000 °C and the extent of interfacial reactivity is examined using Fourier transformed infrared spectroscopy, x-ray photoelectron spectroscopy, and scanning transmission electron microscopy/electron energy loss spectroscopy. An explanation of the observed behavior is also proposed for these systems.

11:00am **EM+TF-FrM10 Comparison of the Calculated Electronic Structure of Oxygen and Nitrogen Adsorption onto Ge(100)**, ***S.R. Bishop**, T.J. Grassman, A.C. Kummel,* University of California, San Diego

For high-k dielectrics on Ge(100), a germanium oxynitride (GeON) interface leads to superior C-V characteristics compared to GeO@sub 2@ passivation layers. Experimental studies show GeON is both a better diffusion barrier and surface passivant than GeO@sub 2@. To understand why GeON is an effective passivating layer, it is necessary to first determine the oxygen and nitrogen binding sites independently. STM studies have shown that the initial stage of O and N adsorption is insertion into the backbonds and into the 2x1 surface dimers, while the final stage is Ge displacement by O and N. The clean Ge(100) surface, oxygen adsorption sites, and nitrogen adsorption sites were modeled using density functional theory (DFT). The DFT calculations show that all oxygen insertion and displacement sites leave the near-Fermi level density of states essentially unchanged compared to the clean surface. This is consistent with O atom insertion and displacement creating no new unfilled dangling bonds. In contrast, the insertion and adsorption sites for nitrogen all create new electronic states in the near-Fermi level region, consistent with nitrogen atoms making two bonds to the surface, but retaining a half-filled dangling bond. However, the Ge-N bonds were found to be stronger than the Ge-O bonds, consistent with GeON being more effective than GeO@sub 2@ as a diffusion barrier. Since the efficiency of GeON as an electronically passivating layer is not intrinsic to its chemisorption states on Ge(100), it may be related to the nitrogens' ability to be electronically passivated by hydrogen. The DFT calculations show that even though N atom displacement of Ge creates states near the Fermi level, hydrogen passivation greatly reduces or eliminates the density of those states.

11:20am **EM+TF-FrM11 Thermal Stability of High-k Dielectrics on Ge(001)**, *F.S. Aguirre-Tostado, M.J. Kim,* ***R.M. Wallace,*** University of Texas at Dallas*; R. Sreenivasan, K.-I. Seo, C.O. Chui, K.C. Saraswat, P.C. McIntyre,* Stanford University*; F.A. Stevie, R. Garcia, Z. Zhu, D.P. Griffis,* North Carolina State University

The use of high-mobility channel materials, such as SiGe and Ge has attracted substantial interest as a means to maintain integrated circuit scaling and performance. A necessary requirement for a MOSFET application is a stable gate dielectric which can be integrated into an appropriate CMOS process flow. High-k dielectrics, such as ZrO@sub 2@ and HfO@sub 2@ have been previously reported for this application with promising electrical results.@footnote 1,2,3@ This paper will describe thermal stability studies of these high-k dielectrics on Ge(001) using in-situ ARXPS and SPM analysis in conjunction with backside SIMS@footnote 4@ and HRTEM analysis. The extent of Zr, Hf and Ge interdiffusion is examined with oxide or oxynitride interfacial layers. Corresponding electrical characterization of the associated devices will also be described in view of the thermal budget where the maximum process temperature is ~500°C. @FootnoteText@@footnote 1@K.I. Seo, P.C. McIntyre, S. Sun, D.I. Lee, P. Pianetta, K.C. Saraswat, Appl. Phys. Lett. 87 (2005) 042902. @footnote 2@D. Chi, C.O. Chui, K.C. Saraswat, B.B. Triplett, P.C. McIntyre, J. Appl. Phys. 96 (2004) 813. @footnote 3@C.O. Chui, H. Kim, P.C. McIntyre, K.C. Saraswat , IEEE Elec. Dev. Lett. 25 (2004) 274. @footnote 4@C. Gu, et. al., J. Vac. Sci. Technol. B22, 350 (2004).

11:40am **EM+TF-FrM12 Oxidation Properties of Al-nanostructures on Si Surfaces**, ***P. Morgen,*** University of Southern Denmark, Denmark*; C. Janfelt,* University of Copenhagen, Denmark*; K. Pedersen,* University of Aalborg, Denmark*; Z.S. Li,* University of Aarhus, Denmark

We have explored the oxidation properties of different nanostructures of Al formed by deposition of Al on Si surfaces with surface sensitive techniques to reveal the differences in reactivity between differently organized nanostructures of Al on these surfaces. In a parallel effort some of these reactions have been modeled with surface electronic structure calculations simulating STM and photoemission spectra, based on the DFT method. Recently several theorists have looked at the initial phases of oxide formed during exposure of Al to oxygen, and found these to differ from bulk Al-oxide. Here we discuss the results for the oxidation of Al on Si (111) and Si (100) in quantities of less than a monolayer as deposited and after annealing of these systems. For the un-annealed systems we discover a route to control the formation of Al-oxide on top of Si with a sharp unmixed interface, while the reactions of the annealed systems show

mixing and enhanced reactivity of the Si surface to oxygen. Ultrathin films of Al on top of Si oxidize at room temperature and at elevated temperatures as a self limiting process, like Si itself. The structure of this oxide includes Al with a coordination number of four.

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