Tuesday Morning, November 10, 2009

Electronic Materials and Processing
Room: B1 - Session EM2-TuM

Complex and Multifunctional Oxides
Moderator: J.D. Phillips, The University of Michigan

8:00am **EM2-TuM1 Electrical Properties of HfO_2 Thin Films Made by RF Sputtering**, ***B. Aguirre***, *R.S. Vemuri, D. Zubia*, University of Texas at El Paso, *W. Jiang, M.H. Engelhard, V. Shutthanandan*, Pacific Northwest National Laboratory, *C.V. Ramana*, University of Texas at El Paso

Hafnium oxide (HfO_2), which exhibits a very high dielectric constant (*k*) and large bandgap, is considered as a next-generation high-*k* material for application in complementary metal-oxide-semiconductor (CMOS) technology. However, growth of high-quality HfO_2 layers on Si without the formation of interfacial compounds poses a significant challenging problem. The objective of the present work was to optimize the conditions to grow high-quality HfO_2 nanolayered films on Si(100). In our work, HfO_2 films were grown by RF sputtering of HfO_2 ceramic target at various substrate temperatures (T_s= 30-500 ^oC) and studied their structure and electrical properties. Al/HfO_2/Si capacitive structures were fabricated to obtain a metal-oxide-semiconductor (MOS) configuration to mimic the gate stack of CMOS technology and study the electrical properties. Grazing incidence x-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) measurements indicate that the effect of T_s is significant on the microstructure. HfO_2 films grown at T_s<200 ^oC are amorphous. An amorphous-to-crystalline transition occurs at T_s=200 ^oC. Nanocrystalline HfO_2 films crystallized in a monoclinic structure with a particle size ~20 nm. XPS measurements indicate the high chemical quality of HfO_2 films grown at T_s=30-500 ^oC. The capacitance-voltage characteristics of the Al/HfO_2/Si devices indicate that HfO_2 films grown (or post-deposition annealed) at 400 ^oC exhibit the expected monoclinic-HfO_2 characteristics. HfO_2 films exhibit a direct correlation with the microstructure. The results obtained are presented and discussed in detail.

8:20am **EM2-TuM2 XPS Characterization of Hf-based High-k Oxide/SiO_2/Si Films Stacks**, ***E. Bersch***, *M. Di*, University at Albany, *S. Consiglio, R. Clark, G. Leusink*, TEL Technology Center, America, LLC, *A.C Diebold*, University at Albany

As the MOSFET SiO_2-based gate dielectric layer approaches its fundamental physical limits, the investigation of high-k oxides is ongoing in order to determine which oxides can best continue the scaling of the MOSFET. HfO_2, hafnium silicates and nitrided hafnium silicates are leading candidates due to their relatively large band gaps, thermal stability in proximity to Si and relatively high dielectric constants.

The band offsets between the high-k oxide layers and Si in high-k/SiO_2/Si films stacks are important parameters in that the gate leakage current depends strongly on them. Recent studies by various groups have also shown that the threshold voltage in MOSFETs with high-k gate oxides can be altered by the presence of an additional oxide layer such as La_2O_3 or Al_2O_3.[1-3] In the case of a La_2O_3 interface layer, the flatband voltage shift has been correlated with a shift in the energy level alignment in the high-k gate stack.[4]

We have used a combination of x-ray photoemission spectroscopy (XPS) and spectroscopic ellipsometry (SE) to measure the valence and conduction band offsets (VBO and CBO, respectively) between high-k layers and Si substrates. We will report VBO and CBO values for HfO_2, hafnium silicate and nitrided hafnium silicate films with Si. In addition, we will report measurements of the HfO_2-Si band offsets from HfO_2/La_2O_3/SiO_2/Si film stacks, noting the effect of the La_2O_3 layer.

Analysis of XPS spectra of the Si 2p spectra from HfO_2/SiO_2/Si film stacks will also be reported, which shows that the composition of the SiO_2 layer and the energy level alignment between the SiO_2 and Si layers were affected by the growth of the HfO_2 layer and the annealing of the film stack. These results will be discussed with respect to the band offset measurements for HfO_2 film stacks.

Finally, using angle resolved XPS (ARXPS) data we constructed non-destructive compositional depth profiles using a maximum entropy algorithm. A comparison between thickness values extracted from these depth profiles and thicknesses measured with SE will be presented.

References:

1. P. D. Kirsch *et al*., *Appl. Phys. Lett.*, **92**, 092901 (2008).

2. V. Narayanan *et al.*, *Symp. VLSI Tech.*, 178 (2006)

3 K. Iwamoto *et al., Appl. Phys. Lett.*, **92,** 132907 (2008)

4. K. Kakushima *et al*., *Appl. Surf. Sci*., **254**, 6106 (2008).

8:40am **EM2-TuM3 Enhanced Dielectric Polarizability of Ge Doped HfO_2 Films on Si and Ge**, ***L. Miotti***, *K.P. Bastos, G. Lucovsky*, North Carolina State University, *D. Nordlund*, Stanford Synchrotron Research Lightsource

The use high dielectric constant materials (high-κ) as gate dielectric in complementary metal-oxide-semiconductor devices based on Si and other higher carrier mobility semiconductors has been focus of intense research. So far, hafnium oxide is among the high-κ dielectrics with higher dielectric constant and higher technologic interest. The most common phase of HfO_2 thin films after deposition and processing is monoclinic with a dielectric constant of κ~ 16-20. However, its dielectric constant can be improved by increasing it in its tetragonal (κ~ 30-35) or cubic phase (κ~ 20-25), which are its thermodynamic equilibrium phases at higher temperatures

We report here on the investigation of Ge doping HfO_2 films and its role in stabilizing the tetragonal phase of hafnium oxide phase. The films were deposited by remote plasma enhanced chemical vapor deposition on both Si(001) and Ge(001) substrates. Hf-t-butoxide and GeH_4 were used as source for Hf and Ge, while O_2 as the oxidizing agent. Germanium concentration in the films was determined by Auger electron spectroscopy. Interface reaction was hindered by nitridation of the substrates before the deposition of the films. Conventional x-ray diffraction analysis is not suited to investigate the crystallographic order in very thin films (< 10 nm), as well as those of interest for device applications. Therefore, we probed the local symmetries by x-ray absorption spectroscopy using the beam line 10 in SSRL.

The x-ray absorption spectra for 2 and 5 nm thick HfO_2 films deposited on Si with 0, 5, or 15 at.% Ge, as well as the second derivative of these spectra was studied. Based on previous studies of HfO_2 films on Si, the shape of the transitions to the E_g and T_{2g} states of the 5 nm thick film without Ge doping corresponds to a monoclinic phase with a different Jahn-Teller distortion than the trigonal. A significant change in these features is observed when the film is doped with 5 at.% Ge. In this case the E_g and T_{2g} transitions correspond to a tetragonal symmetry. Higher germanium doping leads to a mixture of monoclinic and tetragonal phases causing a broadening of the absorption spectra. There is not significant difference in the absorption spectra for the 2 nm thick films with different doping, indicating that the Ge stabilization of a tetragonal phase can only be achieved above a critical thickness.

The mechanism that stabilizes the tetragonal phase of HfO_2 using a tetravalent dopant is significantly different from that associated with trivalent impurities as yttrium, which involves oxygen vacancies. This mechanism results in decrease of the c/a ratio with no vacancies involved.

9:00am **EM2-TuM4 Correlated Oxide Heterostructures**, ***R. Ramesh***, The University of California, Berkeley **INVITED**

Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. The basic materials physics of such materials provide the ideal playground for interdisciplinary scientific exploration. Over the past decade we have been exploring the science of such materials (for example, colossal magnetoresistance, ferroelectricity, etc) in thin film form by creating epitaxial heterostructures and nanostructures. Among the large number of materials systems, there exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics. Using our work in the field of ferroelectric and ferromagnetic oxides as the background, we are now exploring such materials, as epitaxial thin films as well as nanostructures. Specifically, we are studying the role of thin film growth, heteroepitaxy and processing on the basic properties as well as magnitude of the coupling between the order parameters. In this talk I will describe to you some aspects of such materials as well as the scientific and technological excitement in this field.

9:40am **EM2-TuM6 Polarization-dependent Electron Tunneling Into Ferroelectric Surfaces**, ***P. Maksymovych***, *S. Jesse*, Oak Ridge National Laboratory, *P. Yu, R. Ramesh*, University of California, Berkeley, *A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Electron tunneling underlies numerous devices relevant to information technology and has been proposed in future energy harvesting and quantum computing applications. Replacing a conventional insulator in the tunnel junction with an electronically correlated material can yield new types of electronic functionality. In one such concept, dubbed ferroelectric tunneling, the tunneling barrier height is controlled by the polarization of a ferroelectric oxide, enabling non-volatile conduction states that can be switched with electric field. Although ferroelectric tunneling has been

thoroughly theorized, a convincing experimental demonstration of this phenomenon is still lacking. The key challenge is to find a material system that simultaneously satisfies the dimensional constraints for tunneling and ferroelectricity, as well as to assure that the conductance is not dominated by extrinsic effects of charge injection and filamentary conduction, which is ubiquitous in complex oxides.

In this talk we will demonstrate a highly reproducible polarization control of local electron transport through epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ films. Despite being 30-50 nm thick, conductive atomic force microscopy revealed that the films possessed spatially and temporally reproducible local conductivity in the regime of Fowler-Nordheim electron tunneling. This is likely due to a strong electric field in the sub-surface region (excess of 10^6 V/cm) created by the relatively sharp metal tip. Local I-V characteristics exhibited strong hysteretic behavior across the surface. By combining conducting atomic force microscopy with piezoresponse force microscopy, we have, for the first time, directly correlated local events of ferroelectric and resistive switching [1]. The large spontaneous polarization of PZT produced as strong as 500-fold enhancement of FN-tunneling conductance upon ferroelectric switching, sufficient to demonstrate a local non-volatile memory function. The physical mechanism of the observed effect was traced to the polarization-dependence of the height and possibly width of the metal-ferroelectric Schottky barrier.

By observing the role of inherent disorder in ferroelectrics and comparing films grown on different electrode materials, we have shown that the switching voltage and the magnitude of conductance hysteresis are subject to electrostatic control via ferroelectric switching. Variable-temperature measurements and local effects due to dielectric non-linearities will also be discussed.

[1] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, S. V. Kalinin, Science (2009) *in press*.

10:40am **EM2-TuM9 XAS and XPES Studies of Strongly Correlated Ti d-states in $Gd(Sc_{1-x}Ti_x)O_3$,** ***G. Lucovsky,*** North Carolina State University, *C. Adamo,* Penn State University, *D.L. Schlom,* Cornell University, *K.B. Chung*, North Carolina State University

There is considerable interest in complex oxides comprised of transition metal, TM, and lanthanide rare earth, LRE, atoms with room temperature magnetic properties that can modulated by electrical input. Ferro- and ferri-magnetic properties require strongly correlated spin sub-bands derived from TM(LRE) d(f)-states, and have been reported in elemental oxides: CrO_2 and Fe_3O_4, and EuO_2. Strongly correlated bands are created by a double exchange mechanism requiring a transition to a metallic state. The incorporation of tetravalent Ti into a d^0 complex oxide with trivalent Gd and Sc, requires that Ti be in a formal trivalent valence state, Ti^{3+}. Alloying with Ti then introduces a d^1 occupied state into the complex oxide host in direct proportion to the Ti content.

$Gd(Sc_{1-x}Ti_x)O_3$ alloys > 5 nm thick with x = 0.0, 0.01, 0.05, 0.18 and 0.25 were deposited at room temperature in an UHV system onto (i) $LaAlO_3$ substrates for epitaxial growth, and (ii) superficially oxidized Si(001) to produce nano-grain films. As-deposited nano-grain dimensions are 2-2.5 nm, and are too small for Jahn-Teller distortions and spin ordering of Ti alloy atoms. The correlation exchange energy for spin correlated bands is obtained from room temperature films on Si is approximately equal to the energy difference between the localized Ti impurity state energy and Sc band edge d-state.

A compositionally dependent insulator/metal transition is reported for the first time in $Gd(Sc_{1-x}Ti_x)O_3$ alloys for x > 0.16, and is attributed with a correlated Ti d-state band. This insulator to metal transition is identified by X-ray absorption spectroscopy, XAS, extending into the pre-edge regime for X-ray energies <530 eV. Annealing at 900°C in Ar increases grain size enabling Jahn-Teller distortions, and results in an insulator to metal transition evidenced by opening of a gap between oppositely directed Ti spin states. This insulator to metal transition is also observed in as-deposited epitaxial films as well, and consistent with percolation theory, only if the Ti concentration exceeds a critical concentration of ~16.5 %, as in the 18 and 25 % alloys. Differentiation of XAS spectra indicates ferrimagnetism, with a second partially occupied spin band. As predicted by theory, the separation of these spin bands is the same as the correlation exchange energy obtained from the Ti impurity band energy.

This transition is also observed in X-ray photoemission spectroscopy, XPES. The dominant correlated spin band is below the $Gd(Sc_{1-x}Ti_x)O_3$ alloy Fermi level energy in the XPES spectra, and the oppositely directed spin band is at the Fermi level energy.

11:00am **EM2-TuM10 $ZnO/LiNbO_3$ Heterojunctions: A Candidate System For Multifunctional Oxides,** ***E. Cagin,*** *J.D. Phillips*, University of Michigan, Ann Arbor

Ferroelectric/semiconductor heterostructures are desirable for multifunctional devices using the charge of a ferroelectric material to manipulate the conductivity of a semiconductor. The quality of the ferroelectric/semiconductor interface is critical for maintaining a significant ferroelectric polarization charge density, and coupling this charge density into the semiconductor. Therefore, materials must have excellent chemical and structural compatibility. ZnO and $LiNbO_3$ may provide the desired characteristics based on the crystalline compatibility of the materials, excellent semiconducting properties of ZnO, and excellent ferroelectric properties of $LiNbO_3$. In this work, the structural and electrical characteristics of ZnO thin films deposited on z-cut $LiNbO_3$ substrates by pulsed laser deposition will be presented and compared to ZnO thin films on c-plane sapphire substrates. In all experiments, preferentially-oriented c-plane ZnO thin films were obtained based on x-ray diffraction measurements.

Hall effect measurements demonstrate a background carrier concentration in ZnO of n=2. $6x10^{17}cm^{-3}$ for $ZnO/LiNbO_3$, and an order of magnitude decrease of $n=3.0x10^{18}cm^{-3}$ for ZnO/sapphire. Similarly, an improved electron mobility of μ=36 cm^2/Vs is observed for $ZnO/LiNbO_3$ in comparison to μ=21 cm^2/Vs for ZnO/sapphire. The reduced carrier concentration and improved mobility are attributed to a depletion layer at the $ZnO/LiNbO_3$ interface induced by polarization charge. The temperature dependence of electron transport in ZnO thin films will also be presented to examine the influence of polarization charge induced by the pyroelectric effect in $LiNbO_3$.

11:20am **EM2-TuM11 The Study of Electrical and Structural Properties of SiO_2 Film Containing Metal oxide using Organosiloxane-based Silica Precursor,** ***K. Watanuki,*** *A. Inokuchi,* Tohoku University, Japan, *A. Banba, H. Suzuki, T. Koike, T. Adachi,* Ube-Nittou Kasei Co., Ltd., Japan, *A. Teramoto, Y. Shirai, S. Sugawa, T. Ohmi*, Tohoku University, Japan

High quality SiO_2 film formation is important for many applications as electrical insulator films, protective films for semiconductor, alkali-dissolution barrier films and antireflection films on the glass. In some of applications, the electrical property of the films plays an important role. Various techniques have been used thus far in preparing SiO_2 films. Especially, in various techniques, sol-gel technique has significant advantage compared with other techniques with uniformity of thickness, damage free, easy coating of large surfaces, homogeneous multi-component oxide films, controllability of compositions, and potential industrial application. So, in this work, we have evaluated the electrical and structural characteristics of SiO_2 film using organosiloxane-based silica precursor. And we have evaluated the influence of additives to organosiloxane-based silica precursor, such as TiO_2, HfO_2, Ta_2O_5, ZrO_2 and several kinds of metal oxide components on the electrical and structural property of these SiO_2 base insulator films.

The organosiloxane-based sol-gel material investigated here is derived from the mixture of tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) by changing the molar ratio of TEOS/MTMS. In the case of the addition of metal oxide to SiO_2 matrix, such as TiO_2, HfO_2, Ta_2O_5, ZrO_2 and several kinds of metal oxide, metal alkoxides such as tetraisopropoxytitanate (TPOT) were added in the concentration ranging from 1 to 15 mol %. In order to evaluate the electrical property of films, we fabricated MOS (Metal-Oxide-Silicon) devices.

By controlling mixing molar ratio between TEOS and MTMS in the sol-gel precursor, the dielectric constant of films can be controlled. This sol-gel precursor was prepared not only of perfect silica film but also a dense film through optimized conditions such as the pre-baking for 5 min at 130˚C, N_2 ambience low pressure gas removing process continuously increasing the temperature up to 900˚C, and oxidation process using O_2/H_2O at 900˚C. In this study, the influence of additives to the sol-gel precursor was examined on the structural and electrical property of the SiO_2 based films derived from the sol-gel precursor. The breakdown voltages of the resultant films were effectively improved by adding a small amount of metal oxide such as TiO_2, HfO_2, Ta_2O_5 and ZrO_2. It was found that the SiO_2 based film derived from the sol-gel precursor added with metal oxide components, such as TiO_2, HfO_2, Ta_2O_5 and ZrO_2, had excellent uniformly-structured Si-O-Metal bond and that the electrical insulation property of the film was improved by the concentration of metal oxide additives.

Authors Index

Bold page numbers indicate the presenter