Thin Film
Room: 104 A - Session TF+AS+EM+NS+SS-ThM

Thin Film: Growth and Characterization I
Moderator: S.M. Rossnagel, IBM Research Division, T.J. Watson Research Center

8:00am **TF+AS+EM+NS+SS-ThM1 Understanding Strongly Correlated Complex Oxides through Epitaxial Control**, ***T.Z. Ward***, Oak Ridge National Laboratory **INVITED**

The strong electronic correlations arising from overlapping spin-charge-orbital order parameters in complex oxides are of fundamental importance to many desirable characteristics such as the metal-insulator transition, colossal magnetoresistance, and high T_C superconductivity. By selectively tuning the elastic energy in manganite films through epitaxial strain and noble ion implantation, we investigate the influence of isotropic and anisotropic stress/strain on each of the three crystal axes. From this, we can gain a much deeper understanding of how orbital overlaps and occupation act to drive emergent mesoscopic behaviors. We will discuss recent work on $La_{1-x}Sr_xMnO_3$ (LSMO) and $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ (LPCMO) single crystal thin films in which we find many different avenues to tune critical temperatures and magnetoresisitve properties by controlling lattice deformations. Quantum Monte Carlo and percolation models are presented as a means of understanding the role of orbital degeneracy and electronic phase competition in driving macroscopic electron transport and magnetization. These open the door to bridging fundamental discoveries to creation of functional devices. Supported by the US DOE Office of Basic Energy Sciences, Materials Sciences and Engineering Division.

8:40am **TF+AS+EM+NS+SS-ThM3 Tracing the History of Inorganic Thin Films from ~2500 BC to the Early 1900s AD**, ***J.E. Greene***, University of Illinois, Linköping University, National Taiwan University of Science and Technology **INVITED**

Gold was likely the first metal discovered by man, more than 11,000 years ago. However, unlike copper (~9000 BC), bronze (~3500 BC), and wrought iron (~2500-3000 BC), it was too soft for use as tools and weapons. Instead, gold was used for decoration, religious artifacts, and commerce. The earliest documented inorganic thin films were gold layers, < 3000 Å thick, produced chemi-mechanically by Egyptians more than 5000 years ago. Examples, gilded on statues and artifacts (requiring interfacial adhesion layers), were found in early stone pyramids dating to ~2650 BC in Saqqara, Egypt. Spectacular samples of embossed Au sheets date to at least 2600 BC. Fatty-acid-based monolayers were deposited in King Hammurabi's time (~1800 BC, Mesopotamia); modern experiments were carried out much later by Ben Franklin, Lord Rayleigh, and Irving Langmuir. Although there is forensic archeological evidence for electroplating as early as the first few centuries BC, no written evidence survived. The earliest published electroplating experiments were ~1800 AD following the invention of the dc electrochemical battery by Volta. Chemical vapor deposition (CVD) of metal films was reported in 1649. Sols were produced in the mid-1850s (Faraday) and sol-gel films synthesized in 1885.

Vapor phase film growth including sputter deposition (Grove, 1852), arc deposition ("deflagration," Faraday, 1857), atmospheric plasmas (Siemens, 1857), plasma-enhanced CVD (1869, Berthelot), and evaporation (Stefan, Hertz, and Knudsen, 1873-1915) all had to wait for the invention of vacuum pumps whose history ranges from ~1650 for mechanical pumps through ~1865 for mercury pumps that could produce ballistic pressures in small systems. The development of the science of crystallography, leading to Miller indices (1839) for describing orientation and epitaxial relationships in modern thin film technology, was already well advanced by the 1780s. The starting point for the development of heterogeneous thin film nucleation theory was provided by Thomas Young (contact angle equation) in 1805.

While an historical road map tracing the progress of thin film technology is interesting in itself, the stories behind these developments are even more fascinating and provide insight into the evolution of scientific reasoning.

9:20am **TF+AS+EM+NS+SS-ThM5 Metal-Insulator Transition Induced in $SrVO_3$ Thin Films**, ***M. Gu***, *S.A. Wolf*, *J.W. Lu*, University of Virginia

Metal-insulator transition (MIT) in strongly correlated oxides has been an intriguing topic of condensed matter physics over many decades. $SrVO_3$ (SVO) with a $3d^1$ electronic configuration for vanadium is a typical strongly correlated system for studying MIT. High quality epitaxial SVO thin films of various thicknesses were grown on (001)-oriented LSAT single crystal substrates by using a novel pulsed electron-beam deposition (PED) technique. Thick SVO films (~25 nm) exhibited metallic behavior with the electrical resistivity following the T^2 law that corresponds to a Fermi liquid system, the resistance ratio R(300K)/R(2K) was ~1.6. We observed a temperature driven MIT in SVO films with thicknesses below 6 nm. The emergence of this MIT can be attributed to the reduction in the effective bandwidth due to a crossover from a three-dimensional metal to a two-dimensional insulator. We also synthesized $SrTi_{1-x}V_xO_3$ ($0 \leq x \leq 1$) thin films with thicknesses of ~15 nm to study the chemical doping of Ti^{4+} ions in the SVO system. The films with high vanadium content ($x > 0.7$) were metallic following the T^2 law, and the films with low vanadium content ($x < 0.7$) were semiconducting following the variable range hopping mechanism. The x = 0.7 film showed a temperature driven MIT at ~100K. The observed MIT induced by the substitution of Ti^{4+} ions for V^{4+} ions could be interpreted by the induced Anderson localization that trapped the electrons below a mobility edge.

9:40am **TF+AS+EM+NS+SS-ThM6 Bi-Chromatic Far-Field Optical Probing the Percolative Metal-Insulator Transition in VO_2 Thin Film**, ***L. Wang***, *I. Novikova,* The College of William and Mary*, J.M. Klopf, S. Madaras,* Thomas Jefferson National Accelerator Facility*, E. Madaras,* NASA Langley Research Center*, G.P. Williams,* Thomas Jefferson National Accelerator Facility*, R.A. Lukaszew*, The College of William and Mary

Vanadium dioxide (VO2) is a prototype of a highly correlated electron material exhibiting a metal-insulator transition (MIT) that can be thermally, electrically or optically controlled. Using near field optical techniques it has recently been shown that the thermally induced MIT in VO2 thin films is initiated by nucleation of nanoscale metallic puddles in the insulating host. Here we exploit these microscopic changes in phase-composition at the onset and during the MIT on a VO2 thin film sample by observing their effect on the optical properties using far-field infrared (IR) and broadband coherent Terahertz (THz) light optical techniques. We model the transition and are able to accurately describe it particularly regarding the different temperatures recorded at the onset of the MIT depending on the probe used. Further, we compare the optical and DC transport responses, and our findings and modeling settle the question regarding the different transition temperatures observed in each case on the same sample under thermally induced MIT. Finally, we show that Mie scattering explains the observed wavelength scaling dependence of the optical response as function of temperature near the MIT.

10:40am **TF+AS+EM+NS+SS-ThM9 Magnetron Deposition of IGZO Thin Films Utilizing dc, Pulsed dc and Bipolar Power Supply**, ***P. Baroch***, *J. Rezek, J. Houska,* University of West Bohemia, Czech Republic*, P. Ozimek, A. Klimczak*, Huettinger Electronic

Transparent semiconducting amorphous indium gallium zinc oxide (IGZO) films have attracted great attention due to their excellent electrical properties and possible utilization in thin film transistors or in photovoltaic applications. It is known that the properties of IGZO films prepared by magnetron sputtering are highly sensitive to process parameters, especially to oxygen partial pressure. In this study we have focused on the comparison of various types of power supplies with precise control of process parameters in order to optimize electrical and optical properties of the IGZO thin films. We employed dc and pulsed dc power supplies for single magnetron sputtering and bipolar and mid frequency sine wave power supplies for dual magnetron sputtering. All power supplies were equipped with advanced process stabilization solutions, ultra-fast arc management characterized by very low stored energy, and a digital control platform enabling highly flexible software algorithms design. Magnetrons were equipped either with ceramic InGaZnO targets or with metallic InGaZn targets. A novel fast process control system was used in order to precisely control deposition conditions during reactive magnetron sputtering of IGZO films from metallic targets. It is shown that the electrical resistivity can be effectively controlled in the wide range from 10^{-3} to 10^5 Ω.cm and the field effect mobility can reach values up to 40 cm^2/V.s at a film thickness of 270 nm. In parallel to the difference between individual power supplies (sputtering techniques), the effect of the discharge power and the oxygen partial pressure on deposition rate, optical and electrical properties and film structure will be discussed in detail.

11:00am **TF+AS+EM+NS+SS-ThM10 Structure and Optical Properties of Nanocrystalline Hafnium Oxide Thin Films Made by Sputter-Deposition**, ***M. Vargas***, *C.V. Ramana*, University of Texas at El Paso

Hafnium oxide (HfO_2) is a unique material characterized by excellent chemical and physical properties. It is a wide band gap (5.5 eV) material,

which makes it attractive for optoelectronics since it transparent from the ultraviolet to the mid-infrared region. Being a promising high-*k* dielectric, HfO_2 has a strong potential to replace silicon oxide as the insulator in CMOS devices. HfO_2 exhibits various polymorphs; the thermodynamic stability and phase existence depends on the temperature and pressure conditions. Controlled growth and manipulation of specific crystal structures of HfO_2 at the nanoscale dimensions has important technological implications. The present work entails a detailed analysis of growth behavior, microstructure, and optical properties of monoclinic HfO_2 films as a function of growth temperature. In addition, the effect of post-deposition annealing temperature was also studied. HfO_2 thin films were grown by RF magnetron sputtering onto silicon (100) and quartz substrates by keeping power, pressure, and flow of Ar and O_2 and their ratio (70:30) constant, but varying growth temperature from room temperature to 600 C. A thorough characterization was performed through scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and grazing incidence x-ray diffraction (GIXRD). Optical properties were evaluated using spectrophotometric and ellipsometry measurements. GIXRD data revealed a well oriented structure along (-111) as temperature increases, and an evident crystallization temperature at 300 C. The grain sizes measured were in the range of 15 to 20 nm; grain sizes increased with temperature. While SEM and AFM analyses also indicate the grain size with increasing temperature, roughness of the films exhibits a decreasing tendency with increasing temperature. Optical data revealed a double band gap for temperatures higher than RT as well as an increase in band gap with increasing growth temperature. The band gap for at HfO_2 thin films grown at RT was found to be 5.7 eV. The band gap increased to values of ~6.2 eV with increasing growth temperature. A correlation between growth conditions, microstructure and optical properties of nanocrystalline HfO_2 thin films is discussed.

11:20am **TF+AS+EM+NS+SS-ThM11 Studies of Electrical and Surface Properties of High-k Dielectric Gate formed by Al_2O_3, HfO_2, $Al_xHf_yO_z$ and AlHfON on Silicon via Atomic Layer Deposition***, **V. Ou**, Y.S. Lin, R. Candler, S. Franz*, UCLA

In order to meet the increasing demand for high frequency electronic devices, the physical dimensions of MOSFETs have been continuously scaled down to nanoscale. However, one of the bottlenecks we encountered during the down-scaling process is the tunneling current leakage at gates. SiO_2, the most commonly used traditional gate dielectric experiences an appreciable amount of tunneling current when gate thickness is below 1-1.2 nm. The leakage greatly degrades the performance of nanoelectronics. Therefore, we propose using high-k dielectrics to replace SiO_2, which can effectively limit the tunneling leakage without losing the current control at gates. Our research has mainly focus on Al_2O_3, HfO_2 and $Al_xHf_yO_z$ deposit on silicon via Atomic Layer Deposition. The Aluminum to Hafnium ratio in the oxide is tuned to maximize the electrical and physical properties of the film. We expect $Al_xHf_yO_z$ to have a better interface than HfO_2 and an intermediate band-gap between Al_2O_3 and HfO_2, as well as better thermal stability. The electrical properties of each oxide will be characterized by fabricating transistors with gate oxide thicknesses of 5, 10, and 15 nm. In addition to the C-V and I-V measurements for capacitors and transistors, the films will be characterized by XPS, AFM, and spectroscopic ellipsometry. To improve the electrical property of the film, we will incorporate N into the high-dielectric films using Plasma ALD. Finally, the effects of various annealing and deposition temperatures at the silicon-oxide interface will be studied using TEM.

11:40am **TF+AS+EM+NS+SS-ThM12 TiO_2 Film Crystallization by Post-Deposition Annealing***, **A. Henegar**, T. Gougousi*, University of Maryland, Baltimore County

Optical and electrical properties of TiO_2 thin films are largely effected by film morphology. TiO_2 usually crystallizes into anatase or rutile phase. The rutile phase is generally stable while the anatase phase is difficult to produce in pure form through annealing. TiO_2 thin films were grown by atomic layer deposition (ALD) on Si (100) surfaces using tetrakis(dimethylamino) titanium (TDMAT) and H_2O. Films were grown at every 50°C increment from 100 to 300°C approximately 100 nm thick, determined by nominal growth rates derived from spectroscopic ellipsometry (SE) measurements. The growth rate varied from 0.4Å/cycle at the ALD optimal temperature of 200°C to 1.2Å/cycle at 300°C. Films were annealed post-deposition at temperatures of 500°C, 700°C and 900°C for 3, 5 and 10 minutes in an argon environment using a rapid thermal annealer. Characterization was completed using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). FTIR measurements indicate that the as-deposited films have an amorphous structure. Annealed films exhibit various crystallization to rutile phase, anatase phase, or a mixture of the two phases, depending on the deposition and post-deposition annealing conditions, as confirmed by XRD. Specifically, TiO_2 films grown at 100°C and annealed for 10 minutes at 900°C exhibit only amorphous and anatase phase TiO_2. It is shown that TiO_2 crystallinity can be tuned between amorphous, anatase and rutile phases by controlling the deposition temperature and post-deposition annealing parameters.

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