

Monday Morning, October 31, 2011

Thin Film Division

Room: 107 - Session TF-MoM

Thin Films: Growth and Characterization I

Moderator: J.M. Fitz-Gerald, University of Virginia

8:20am **TF-MoM1 Heavy Ion Irradiation Effects on Ti/Al Multilayer Thin Films**, R.S. Vemuri, The University of Texas at El Paso, T. Varga, S.V. Shuthanadan, S.V.N.T. Kuchibhatla, M.H. Engelhard, P. Nachimuthu, C.H. Henager, C.M. Wang, S. Thevuthasan, Pacific Northwest National Laboratory, C.V. Ramana, The University of Texas at El Paso

There has been growing interest in thin bi-metallic multilayer films for the usage under extreme radiation conditions because of their radiation healing properties. Recent discovery and research indicate that materials can be hardened against radiation damage by building nanolayered structures with an optimized layer thickness to increase point defect recombination relative to a non-layered structure and that can self-heal. In this study, we investigate whether the internal interfaces can be manipulated at the nanoscale to enhance dynamic recombination of radiation-produced defects, or self-healing, so as to dramatically reduce radiation damage without compromising other properties using Ti/Al multilayer films.

Ti/Al multilayer films were fabricated on Si (100) and epi polished MgO (100) substrates using DC magnetron sputtering and Molecular beam epitaxy (MBE). The growth parameters for each method, for sputtering – pressure, power and substrate temperature deposition rate; and for MBE-deposition rate and substrate temperature were optimized to achieve high-quality thin films. The films were characterized using x-ray diffraction (XRD), x-ray reflectivity (XRR), Rutherford backscattering spectrometry (RBS), and x-ray photoelectron spectroscopy (XPS) measurements. The films show mostly polycrystalline structure with no elemental interdiffusion at the interfaces. Detailed structural and compositional analysis was also performed using high resolution TEM/STEM and atom probe tomography (APT). The films were irradiated using 1-8 MeV Au ions to understand the radiation effects. The damage peak, stopping range and ion distribution were simulated using binary collision approximation based Monte Carlo method (SRIM software program). Au ion energies, estimated from the simulation, were used to position the damage peak at the interested interfaces and away from the interfaces to obtain the complete picture at the interfaces and in the bulk of the films. The interface and crystal lattice damage, amorphization, and defect density were studied by RBS, HAADF-STEM and APT, and compared with those results from the pristine samples. The relationships between film properties and radiation healing characteristics will be presented and discussed.

8:40am **TF-MoM2 Flux and Surfactant-Assisted Physical Vapor Deposition: New Approaches for Improving Complex Oxide Thin Film Growth**, J.-P. Maria, E.A. Paisley, B.E. Gaddy, North Carolina State University, M.D. Biegalski, Oak Ridge National Laboratory, D.L. Irving, A.R. Rice, R. Collazo, Z. Sitar, North Carolina State University **INVITED**

Epitaxial integration of complex oxides with wide band gap polar semiconductors such as GaN (0002) presents the possibility for high-power, high-frequency, and high temperature GaN electronics by virtue of 2-D charge carriers at polar interfaces and possible access to non-linear dielectric properties. This work describes synthesis and characterization of such thin film heterostructures by MBE, with specific attention given to controlling film growth. Our previous work has shown growth of high-quality MgO (111) and CaO (111) films on GaN with measured valence band offsets > than 1 eV and conduction band offsets ~ 3.2 eV (MgO) and ~2.5 eV (CaO). However, the terminal 3D rocksalt growth surface is determined by the tendency for the high-energy (111) polar orientation to form (100)-oriented low-energy facets, and the interfacial symmetry between cubic MgO and hexagonal GaN. Therefore, realizing smooth oxide films on GaN requires the ability to overcome the rocksalt (001) faceting tendency through a surfactant growth method. In this presentation we will discuss a newly-developed surfactant approach to MBE growth of rocksalt oxides utilizing water vapor to hydroxylate CaO and MgO (111) surfaces *in situ*, which changes the equilibrium habit from cubic to octahedral, eliminating the (100) faceting tendency. RHEED oscillations and AFM images of these films show 2D growth, suggesting that altering the surface chemistry during growth plays a critical role in determining the surface orientation. We demonstrate through electrical property measurements the impact of smooth (111) rocksalt surfaces as leakage current densities for thin CaO films are reduced by two orders of magnitude when films of equivalent thickness are grown using a 2-D vs. a 3-D mode. Finally, we will present a set of temperature *ab-initio* thermodynamic calculations of CaO

surface energies with and without H-containing terminations that validate the surface-chemical mechanism of facet stabilization.

9:20am **TF-MoM4 Initiated – Chemical Vapor Deposition of Organosilicones: from Growth Mechanism to Multilayer Moisture Diffusion Barriers**, G. Aresta, J. Palmans, M.C.M. van de Sanden, M. Creatore, Eindhoven University of Technology, Netherlands

The state-of-the art approach in the encapsulation of high-end devices such as flexible (polymer) solar cells and organic light emitting diodes against water vapour permeation is an organic/inorganic multi-layer system. Although this approach allows increasing the lifetime of the encapsulated device, the optimization of a multi-layer is rather empirical as the mechanisms behind the improvement of the barrier performance are not yet unraveled. In particular, the role of the organic interlayer is rather controversial since effectively it does not act as a moisture vapor barrier, yet its application appears to be fundamental in the multi-layer solution. In this contribution, the role of the organic interlayer is investigated by selecting a system in which the barrier layer, a 100 nm-thick SiO₂ film, is plasma-deposited while the organic interlayer, a 200 nm-thick organosilicon film, is synthesized by means of initiated- chemical vapor deposition, i.e. via thermal decomposition of an initiator molecule promoting the polymerization of 1,3,5-trimethyl-1,3,5-trivinyl-cyclotrisiloxane (V₃D₃) at the substrate.

The implementation of *in situ* (real time) spectroscopic ellipsometry allows following the different growth stages in the V₃D₃ polymerization process. In particular, when applied to the polymer bulk growth, the determination of the growth rate allows monitoring the transition from a kinetic-limited (with activation energy of 65 ± 4 kJ/mol) to a mass transfer-limited regime. Furthermore, the deposition process is found to be monomer adsorption-limited with an activation energy of -39 ± 4 kJ/mol. When spectroscopic ellipsometry is applied to the initial monomer adsorption steps, isothermal adsorption/desorption studies provide insight into the microstructure of the underlying SiO₂ barrier layer, characterized by a residual open porosity in the micro/meso transition region (pore radius ≤ 2nm). The microstructure characterization by means of the above-mentioned studies implicitly points out the role of the i-CVD organic interlayer in multi-layer barrier structures, i.e. the filling of the open micro-meso porosity of the inorganic barrier layer, therefore, improving the intrinsic barrier quality of the underlying SiO₂ film. This outcome nicely correlates with the superior water vapor barrier performances (a barrier improvement factor of 2400 is reported with respect to the pristine polymer) of multi-layers based on the application of i-CVD organic interlayers with respect to fully-PECVD developed multi-layers.

9:40am **TF-MoM5 Processing and Characterization of Iron and Fluorine Co-Doped Ba_{0.6}Sr_{0.4}TiO₃ Thin Films**, F. Stemme, H. Gesswein, C. Azucena, Karlsruhe Institute of Technology (KIT), Germany, M. Szegar, Darmstadt University of Technology, Germany, J.R. Binder, M. Bruns, Karlsruhe Institute of Technology (KIT), Germany

Barium strontium titanate (BST) is a very promising material for tunable microwave applications like phase-shifters and tuneable filters. Due to this the influence of e.g. annealing conditions and processes on thin film properties and their dielectric performance were largely investigated. But very few researchers have tried to change the sputtered BST thin film properties by using different dopants at the same time. Such iron and fluorine co-doped thin films can be achieved by RF magnetron sputtering, with a co-sputter target and a two step annealing process after deposition. The first annealing process provides the crystallinity of the films. In the second annealing process the fluorine co-dopant is introduced into the BST thin films by a diffusion controlled process.

The present contribution focuses on the processing and characterization of the iron doped BST thin films with various amounts of fluorine co-dopant. The characterization of the thin films by X-ray photoelectron spectroscopy (XPS) provides chemical binding states and film composition. XPS and time of flight secondary ion mass spectrometry (ToF SIMS) sputter depth profiles prove the chemical homogeneity and the film thickness. Grazing incident X-ray diffraction (XRD) and Raman spectroscopy validate the crystallinity and the identification of chemical phases. Furthermore film morphology is determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Dielectric measurements, to investigate the influence of the donor and acceptor co-doping on the dielectric performance, were carried out in metal insulator metal (MIM) structures with ground signal ground probes.

10:00am **TF-MoM6 Advances in the Growth of Epitaxial Oxides for Neuromorphic Computing Applications.** *J.D. Greenlee, W.L. Calley, W.A. Doolittle*, Georgia Institute of Technology

Present-day computing devices are approaching performance limits due to excess heat and parasitic capacitance degrading performance. One proposed solution, termed “neuromorphic computing”, is to perform computations similarly to the brain.

A key enabling device for neuromorphic computing is the lithium niobate (LiNbO₂) memristor[1]. Like synapses in the brain, LiNbO₂ memristors can exhibit excitatory or inhibitory behavior. This is due to the ability to produce both n and p-type LiNbO₂ memristors, a unique property for an oxide. As shown in Figure 1, when a voltage is applied across an n-type memristor (left), resistance increases over time, whereas a p-type memristor exhibits decreasing resistance (right). N-type memristors are grown with excess oxygen vacancies while p-type memristors are grown with excess lithium vacancies. N- and p- type films are very conductive, exhibiting resistances of $4.3 \times 10^{-4} \Omega\text{-cm}$ (p-type) and $3.9 \times 10^{-4} \Omega\text{-cm}$ (n-type) with carrier concentrations higher than 10^{21} cm^{-3} and Hall mobilities greater than $8 \text{ cm}^2/\text{V}\cdot\text{s}$.

The epitaxial growth of LiNbO₂ is the enabling technology for the memristors described above. Growths are conducted using an oxy-chloride MBE system in which metal-halide sources interact with lithium and oxygen [2]. Lithium acts as a getter for the chlorine from the metal-halide, and the resulting LiCl is desorbed from the heated growth surface. The bare metal then oxidizes under the application of an oxygen plasma and combines with lithium. This growth chemistry has been used to produce dielectric/ferroelectric lithium niobate (LiNbO₃), semiconducting lithium niobate (LiNbO₂), and lithium cobalt oxide (LiCoO₂).

Insulating LiNbO₃ (Figure 2) and semiconducting LiNbO₂ (Figure 3) are grown using NbCl₅, and the phase of the material is controlled by the niobium to oxygen ratio delivered to the growth surface. Both single crystal LiNbO₃ and LiNbO₂ have been epitaxially grown on Al₂O₃ and SiC. LiNbO₃ is a promising lattice matched, ferroelectric transistor gate high-k oxide for its semiconducting sub-oxide, LiNbO₂. LiNbO₂ has a layered, lithium-intercalated structure [3] (Figure 4). When lithium is removed, holes are introduced which increases the conductivity of p-type material and decreases the conductivity of n-type material, thus producing the memristance effect described herein.

LiCoO₂ is grown on Al₂O₃ using CoCl₂ as the precursor (Figure 5). Like LiNbO₂, LiCoO₂ has a layered structure that facilitates lithium movement. The lattice spacing of LiCoO₂ is closely matched to LiNbO₂ (2.81 Å and 2.91 Å respectively), thus making it an attractive material for heterostructures of lithium-bearing semiconductor materials.

10:40am **TF-MoM8 New Method to Produce High-Quality Epitaxial Ge on Si Using SiO₂-Lined Etch Pits and Epitaxial Lateral Overgrowth for III-V Multijunction Solar Cells.** *D. Leonhardt, S.M. Han*, University of New Mexico

Integrating a high-quality layer of epitaxial Ge on Si has been a longstanding engineering challenge, despite its technological importance. The applications of Ge-on-Si include ‘virtual substrates’ for III-V multijunction solar cells, high-mobility field-effect transistors, and optical interconnects monolithically integrated with Si-based circuitry. The primary difficulties in achieving Ge films of sufficient quality stem from the lattice mismatch that leads to a large density ($> 10^9 \text{ cm}^{-2}$) of threading dislocations (TDs) and the thermal expansion coefficient mismatch between Ge and Si that leads to microcracks or delamination of Ge film upon cooling from growth to room temperature. Herein, we present a new method to reduce the TD density, using a minimal number of standard microfabrication steps. The method begins with growing a 500-nm-thick epitaxial Ge layer on Si. A post-growth anneal step leads to a TD density of approximately $5 \times 10^7 \text{ cm}^{-2}$, as revealed by plan-view transmission electron microscopy (TEM) and etch pit density (EPD) measurements. The close agreement between EPD measurements and TEM shows that the EPD measurements reliably decorate all TDs. Etch pits are created around the dislocation cores in the Ge film. A 15-nm-thick layer of SiO₂ is subsequently deposited on the etch-pit-decorated Ge film. A thin layer of polymethyl methacrylate is then spin-coated onto the sample, which fills the etch pits and planarizes the Ge surface. Next, a reactive ion etching step is used to remove the polymer and SiO₂ from the planar regions of the sample surface surrounding the etch pits. An O₂ plasma is then used to selectively remove the remaining polymer, so that SiO₂ remains only within the etch pits. Lastly, a second layer of Ge is selectively grown on the exposed Ge surface and laterally over the SiO₂-lined etch pits until a fully coalesced Ge film is created. A final polishing step produces an atomically flat continuous Ge film. Ensuing EPD measurements reveal that the density of twin defects and TDs in the upper Ge layer is approximately $1.7 \times 10^6 \text{ cm}^{-2}$, such that the overall defect density is reduced by a factor greater than 30 compared to that in the initial Ge layer. Both theoretical and experimental evidence suggest that the defect

density in GaAs films on Ge/Si must be less than $2 \times 10^6 \text{ cm}^{-2}$ to have a minority carrier lifetime comparable to GaAs films grown on Ge and GaAs substrates. Therefore, our new method of using SiO₂-lined etch pits to block the propagation of TDs in Ge may finally lead to device quality III-V materials integrated on Si substrates.

11:00am **TF-MoM9 Three Dimensional Reciprocal Space Measurements by X-ray Diffraction using Linear and Area Detectors: Application to Texture and Defect Determination in Oriented Thin Films and Nanoprecipitates.** *S. Gaudet, S. Lambert-Milot, P. Desjardins*, École Polytechnique de Montréal, Canada, *K. Dekeyser, C. Detavernier*, Ghent University, Belgium, *J.L. Jordan-Sweet, C. Lavoie*, IBM T.J. Watson Research Center

Very thin films grown or deposited on oriented substrates are often composed of highly oriented phases. Traditional x-ray diffraction approaches, scanning only limited portions of the reciprocal space, can fail to characterize some phenomenon occurring in those thin films. We developed an approach for the fast and efficient measurement of complete volumes of the reciprocal space by x-ray diffraction using linear and area detectors. In this presentation, we show how it allowed a detailed understanding of the solid-state thin film reaction to form contacts on transistors and of the growth of magnetic nanoprecipitates by metalorganic vapor-phase epitaxy. We first explain the procedures and scan strategies required for transforming raw scattering data into three-dimensional maps of the reciprocal space, and we present a complete open source software package for advanced data processing, analysis, and visualization. Case studies, chosen to highlight the overall capabilities of the technique, are then introduced. First, thermal diffuse scattering from a monocrystalline Si substrate is characterized. The presence of lines linking diffraction peaks in reciprocal space reflects the interaction of the x-ray beam with the phonon spectrum of the monocrystal. Second, a detailed investigation of texture in multiphase thin layers permits to reveal the unambiguous presence of fiber, axiotaxial, and epitaxial components in extremely oriented films. The visualization of the entire reciprocal space allowed us to identify unexpected metastable phases that could not be deduced or observed from measurements carried out in the Bragg-Brentano geometry. Finally, we present an investigation of defects in two thin film systems: planar defects in nickel silicide layers formed by solid-state reactions and microtwins in a GaP matrix containing coherent MnP precipitates. In summary, the systematic acquisition of significant volumes of the reciprocal space allows for the observation of behaviors that could otherwise remain undetected when restricting the analysis to typical measurement scans.

11:20am **TF-MoM10 Surface Characterization of Zr/Ti/Nb Tri-layered Films Deposited by Magnetron Sputtering on Si(111) and Stainless Steel Substrates.** *D.A. Tallarico*, Federal University of Sao Carlos, Brazil, *A.L. Gobbi*, Brazilian Synchrotron Light Laboratory, Brazil, *P.I. Paulin-Filho*, Federal University of Sao Carlos, Brazil, *A. Galtayries*, Ecole Nationale Supérieure de Chimie de Paris, France, *P.A.P. Nascente*, Federal University of Sao Carlos, Brazil

Titanium is a metal commonly used in medical implants, due to its interesting properties, such as high mechanical strength, good corrosion resistance in extreme conditions, and excellent thermal stability. Ti-6Al-4V is one of the main biomaterial alloys employed as implants, but the release of Al and V ions is associated to health problems and adverse tissue reactions. A new class of Ti alloys employs Zr for solid-solution hardening and Nb as β phase stabilizer. Metals such as Ti, Nb, and Zr, known as valve metals, usually have their surfaces covered by a thin oxide film spontaneously formed in air. This oxide film constitutes a barrier between the metal and the medium. The Ti-Nb-Zr alloys have mechanical and corrosion resistance characteristics which make them suitable for use as implants. Tri-layered films of Ti-Nb-Zr were deposited on both Si(111) and stainless steel substrates using a DC magnetron sputtering equipment, under an argon atmosphere. The films were deposited in the following manner: a 100 nm thick layer of Nb was deposited on a Si(111) substrate, then a 200 nm layer of Ti was deposited on top of Nb/Si, and lastly a 50 nm layer of Zr was deposited on top of Ti/Nb/Si. A similar Zr/Ti/Nb film was also grown on stainless steel substrate. The structure, morphology, and chemical composition of the films were analyzed by means of X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The XPS results for the Zr/Ti/Nb layers deposited on Si(111) presented a predominance of ZrO₂ on the surface, and Nb₂O₅ and a small quantity of TiO₂. For the layers deposited on stainless steel, only ZrO₂ and a small amount of niobium oxide were detected. The ToF-SIMS results indicated the formation a three-layered film on Si(111), with each metal in a distinct layer and a well-defined interface between the layers, while the deposition on the stainless steel substrate caused slight intermixing at the Nb/Ti and Ti/Zr interfaces. AFM images showed that the Zr/Ti/Nb tri-layer films

presented nanostructured grains and low roughness, with the film deposited on stainless steel having the roughest surface.

11:40am **TF-MoM11 PECVD Synthesis of Hybrid Organic-Inorganic Nanolaminates**, *R. Patel, C.A. Wolden*, Colorado School of Mines

Hybrid organic-inorganic nanolaminates combine the functionality of an inorganic material with the flexibility and mechanical integrity provided by the organic polymer layer. They are integral components in various applications serving as advanced dielectrics, flexible barrier coatings, and as optical components. This work focuses on the low temperature synthesis of alumina/silicone nanolaminates by plasma-enhanced chemical vapor deposition (PECVD) in a single chamber for dielectric applications.

Self-limiting synthesis of alumina was accomplished via pulsed PECVD at the synthesis temperature of ~ 100 °C using trimethyl aluminum (TMA) and oxygen as precursors. The deposition kinetics and film quality were evaluated as a function of precursor exposure, plasma power, substrate temperature, and pulse parameters. Film composition was assessed by using spectroscopic ellipsometry and Fourier transform infrared spectroscopy (FTIR). The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TMA concentration and pulse duration, the depositing rate could be adjusted over a narrow range (1.6 – 2.8 Å/pulse). Alumina films deposited at 105 °C contained a very small concentration of hydroxyl impurities. Polymeric silicone-like coatings were deposited using hexamethyldisiloxane (HMDSO) and oxygen as precursors. A wide range of coatings, from inorganic SiO₂-like films to flexible polymeric films could be deposited by appropriate control of parameters including the rf power, substrate temperature and working pressure. Growth rates as high as 100 nm/min were obtained for polymeric silicone films.

Alumina/silicone nanolaminates were constructed as a function of nanolaminate composition and dyad thickness. Precise control of nanolaminate construction was confirmed through field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The dielectric performance of these structures was examined by using capacitance-voltage and current-voltage measurements. The effective dielectric constant could be controlled by changing the alumina content of the nanolaminates, and modeling these structures as capacitors in series accurately described the observed variations in κ .

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