Thin Film
Room: 111 - Session TF+AS+NS+SA-ThA

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization II
Moderator: Jay Hendricks, National Institute of Standards and Technology

2:20pm **TF+AS+NS+SA-ThA1 Dynamic and Structural Stability of Cubic Vanadium Nitride**, ***Antonio Mei****, University of Illinois at Urbana-Champaign, *O. Hellman,* California Institute of Technology, *N. Wireklint,* Chalmers University of Technology, Sweden, *C.M. Schlepütz,* Argonne National Laboratory, *D.G. Sangiovanni, B. Alling*, Linköping University, Sweden, *A. Rockett,* University of Illinois at Urbana-Champaign, *L. Hultman,* Linköping University, Sweden, *I. Petrov, J.E. Greene*, University of Illinois at Urbana-Champaign

Structural phase transitions in epitaxial stoichiometric VN/MgO(011) thin films are investigated using temperature-dependent synchrotron x-ray diffraction (XRD), selected-area electron diffraction (SAED), and resistivity measurements combined with high-resolution cross-sectional transmission electron microscopy (HR-XTEM) and *ab-initio* molecular dynamics (AIMD). At room temperature, VN has the B1 NaCl structure. However, at temperatures below T_c = 250 K, XRD and SAED results reveal forbidden (00*l*) reflections of mixed parity associated with a non-centrosymmetric tetragonal structure. At $T \leq T_c$, forbidden reflections intensify continuously following the scaling behavior $I \alpha (T_c - T)^{1/2}$. This suggests a transition of second-order character, but the incompatible symmetries of the parent cubic VN (space group) and product tetragonal VN () phases ultimately requires that the structural transition be first order. Resistivity ρ(T) plots between 300 and 4 K consist of two linear regimes resulting from different electron/phonon coupling strengths in cubic and tetragonal VN.

The VN transport Eliashberg spectral function $\alpha^2_{tr}F(\hbar\omega)$, the product of the phonon density-of-states $F(\hbar\omega)$ and the transport electron/phonon coupling strength $\alpha^2_{tr}(\hbar\omega)$, is determined and used in combination with room-temperature inelastic neutron scattering results to establish that while entropy favors the higher-temperature cubic phase, as T is lowered below T_c, tetragonal VN becomes the thermodynamic ground state due to its lower enthalpy. AIMD renormalized phonon dispersion relations are in agreement, showing that the energy of (00*l*) X-point phonons in NaCl-structure VN decreases and eventually becomes imaginary at $T \leq 250$ K. We demonstrate that free energy contributions due to vibrational entropy, often-neglected in theoretical modeling, are essential in understanding the room-temperature stability of NaCl-structure VN, and of strongly anharmonic systems in general.

2:40pm **TF+AS+NS+SA-ThA2 Comparison of Solution Based Aluminum Oxide Phosphate Thin Films Deposited via Spin Coating vs. a Novel Mist Deposition System**, ***Nishit Murari****,* *R.H. Mansergh, Y. Huang, G. Westerfield, D. Keszler, J.F. Conley*, Oregon State University

Solution based spin coating techniques are well known for producing high quality organic as well as inorganic metal oxide thin films. However, spin coating is primarily suitable for planar substrates and lacks the ability to form uniform ultrathin films over large surface areas. In recent years, several alternative mist based deposition techniques have been introduced to enable solution based deposition over large areas and non-planar substrates. Mist deposition involves the creation of a precursor mist and its subsequent condensation on the substrate. Mist deposition techniques to date have been limited by disadvantages such as the requirement for highly volatile precursors and the non-homogeneous distribution of the mist, both of which lead to inferior film thickness uniformity. To address these limitations, we employ a new mist deposition system with a novel mist creation technique consisting of an atomizer with two opposing precursor jets. The unique opposing configuration of the atomizer enables the formation of a highly uniform mist even from low volatility precursors. In this work, we address the question of whether this new mist deposition technique can produce film quality comparable to spin coating technique.

Amorphous aluminum phosphate (AlPO) thin films were deposited via mist deposition using a BENEQ ACS 200-101 as well as standard spin coating. All films were deposited at room temperature and pressure using precursors based on aqueous suspensions of aluminum phosphate inorganic clusters. The inorganic ligands decompose at low temperature with minimal volume change presenting a route to high density films at low temperature. Both mist and spin coating achieve thickness uniformity of 5% across a 150 mm Si substrate. Both techniques result in ultra-smooth films with average surface roughness of less than 1 nm RMS. Variation in film density and roughness as a function of annealing temperature was identical for both techniques. Finally, similar charge transport behavior and dielectric constant were exhibited as a function of anneal temperature.

An aqueous precursor was used in a side by side comparison of spin coating and a novel mist deposition technique. High quality AlPO thin films of similar uniformity, density, roughness, and electrical properties were obtained using both techniques. Based on these results, this novel mist based deposition technique appears to be a promising candidate for the next generation of thin film deposition techniques for large area electronics.

3:00pm **TF+AS+NS+SA-ThA3 Electro-Optic Studies of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ Thin Films Deposited by Chemical Solution Deposition Method**, ***Vaishali Batra****,* *S. Kotru, V.N. Harshan,* The University of Alabama, *M. Varagas, C.V. Ramana*, University of Texas at El Paso

Lanthanum doped lead zirconate titanate (PLZT) of perovskite type crystalline structure is an interesting transparent ferroelectric material due to its large remnant polarization and electro-optic effects, near the morphotropic phase boundary. The excellent optical and electrical properties make it material of choice for applications in MEMS, optical modulators/transducers and smart sensors. Recent studies reveal that this material possesses great potential for use in future photovoltaic (PV) devices which involves combination of optical transparency and ferroelectric properties. The advantage of using this material for PV applications is that the effect can be realized without a need of p-n junction as in semiconductor devices. Additionally the material exhibits bulk PV effect due to internal electric field originating from electric polarization. However, the optimization of processing conditions of deposited films is important to design efficient devices, which require understanding of the structure, its behavior with light, and response to electric field.

Lanthanum-modified lead zirconate titanate (PLZT) thin films with a composition of $(Pb_{0.95}La_{0.05})(Zr_{0.54}Ti_{0.46})O_3$ were deposited on $Pt/TiO_2/SiO_2/Si$ substrates. The films were rapidly annealed in the temperature range of 550 to 750 °C in oxygen ambient to study the effect of crystallization on the electric and optical properties. X-ray diffraction revealed that the post deposition temperature changes the preferential orientation of the films. Optical band gap values determined from UV-visible spectroscopy and spectroscopic ellipsometry for PLZT films were found to be in the range of 3.42-4.00 eV. The optical constants and their dispersion profiles for PLZT films were also determined from SE analyses. PLZT films exhibit an index of refraction ~2.5 (λ=630 nm). The electrical properties were studied using the model for metal-ferroelectric-metal (MFM) heterostructures with Schottky contacts using Au electrodes. High remnant polarization (41.85 $\mu C/cm^2$), low coercive voltage (1.19 V) and high free carrier concentration ($\sim 1.1 \times 10^{18}$ cm^{-3}) were obtained from films annealed at 750 °C. Thus post deposition annealing temperature plays a major role in deciding the electrical and optical properties.

3:20pm **TF+AS+NS+SA-ThA4 Electron Scattering at Surfaces of Expitaxial Metal Layers**, ***Pengyuan Zheng****,* *D. Gall*, Rensselaer Polytechnic Institute

Epitaxial Cu(001) is grown on MgO(001) with different overlayers to demonstrate that electron surface/interface scattering can be engineered by surface doping, causing a decrease in the resistivity. For instance, the resistivity of 9.3-nm-thick epitaxial and polycrystalline Cu layers is reduced by 11-13% when coated with 0.75 nm Ni. This is due to partially specular surface scattering with specularity parameters *p* = 0.3 and 0.15 for the Ni-coated Cu in vacuum and air, respectively, while scattering is completely diffuse (*p* = 0) for a pure Cu surface in air. This is attributed to the suppression of Cu_2O formation, leading to a lower localized density of states (LDOS) at the surface, and therefore less diffuse electron scattering. The change of surface scattering by controlling the LDOS is further confirmed: the sheet resistance of 9.5-nm-thick epitaxial Cu(001) increases by 4-43% if a 0.1-4 monolayer thick Ti coating is added, but subsequent exposure to 37 Pa of O_2 causes a resistivity reduction of 3-24%. This reduction is due to a recovery of specular interface scattering associated with a reduction of the LDOS during Ti oxidation from 15-27.4 to 2.4-6.5 $eV^{-1}nm^{-2}$, as quantified by ab initio calculations. Furthermore the surface scattering effect is found to be orientation dependent. For example, the resistivity of 5-nm-thick epitaxial tungsten layers is two times higher for 001 vs 110 orientated layers. This is due to the anisotropy in the Fermi surface, as indicated by transport simulations based on first-principles band structure calculations, which suggest a 1.5 times smaller size effect for the

* **TFD James Harper Award Finalist**

110 orientation. These epitaxial films were sputter deposited onto Al2O3(11-20) and MgO(001) at 1050 °C and 900 °C, respectively, followed by in situ annealing at 1050 °C for 2 hrs. X-ray diffraction θ-2θ, ω, and φ-scans confirm epitaxy and X-ray reflectivity indicates atomically smooth film-substrate interfaces and smooth film surfaces with a root-mean-square roughness that increases from 0.32±0.05 to 0.81±0.05 nm for W(110) with t = 5.7-39.2 nm, and from 0.21±0.05 to 0.40±0.05 nm for W(001) with t = 4.8-50 nm. In summary, we have systematically shown that (1) surface scattering can be altered by carefully controlling the surface LDOS at the Cu surface or interface with the barrier and (2) the crystalline orientation of interconnect wireswith non-spherical Fermi surfaces is a major factor when considering alterative metals to replace Cu interconnects.

4:00pm **TF+AS+NS+SA-ThA6 Lattice Relaxation in Multilayered $Si_{1-x}Ge_x$/Si (001) Metamorphic Heterostructures**, ***Tedi Kujofsa***, *J.E. Ayers*, University of Connecticut

The inclusion of compositionally-graded metamorphic buffer layers in multilayered heterostructures allows tremendous flexibility designing novel SiGe/Si microelectronic and optical semiconductor devices. For example, advanced CMOS transistors can be fabricated on strain relaxed buffers to obtain enhanced mobility in n-channel and p-channel devices using tensile and compressive strain, respectively. While it is necessary to control the strain in the device layers, it is also desirable to fabricate these structures with low threading dislocation densities and minimum buffer thickness. Thus, understanding lattice relaxation in multilayered and compositionally-graded heterostructures is desirable to provide guidance in designing SiGe/Si devices. This work focuses on the design of the multilayered heterostructures comprising a uniform layer of $Si_{1-x}Ge_x$ (device layer) deposited on a Si (001) substrate with an intermediate compositionally-graded buffer layer of $Si_{1-x}Ge_x$. The objective of this work is to study the relaxation dynamics and misfit dislocations in the device and buffer layer. We present minimum energy calculations and show that for a given device layer with fixed germanium composition and layer thickness, there exists a combination of the buffer layer thickness and compositional grading to provide tight control of the strain in the device layer. Furthermore, we give a simple model describing the strain in the device layer.

4:40pm **TF+AS+NS+SA-ThA8 Growth Stress Evolution in Low Adatom Mobility Fe(Cr) Thin Films**, ***Xuyang Zhou***, The University of Alabama, *T. Kaub, R.L. Martens*, The Univeristy of Alabama, *G.B. Thompson*, The University of Alabama

During the post coalescence portion of thin film deposition, thin film stress is related to the grain size and adatom mobility of the depositing material. This stress state can be regulated by the mobility of atoms into or out of these grain boundaries. Using Fe(Cr) alloy thin films as a case study, the stress evolution during growth was investigated as a function of Cr content up to 8 at.%. During the deposition of the elemental films, each film grew with a tensile stress state on a Si wafer because of their low adatom mobility. Upon alloying 4 at.% Cr to the Fe film, the as-deposited grains grew from ~40 nm (pure Fe) to ~65 nm (Fe-04Cr), resulting in a stress relaxation from ~200 GPa*nm to 50 GPa*nm at a thickness of 300 nm. As the Cr content increased further, the grains refined back towards ~ 50 nm in size resulting in a recovery of the higher tensile stress condition. The reduction of the grain size is contributed to Cr solute segregation to the grain boundaries, clustering, and ultimately precipitation at the boundaries. The real-time stress evolution during growth will be discussed in terms of the inferred microstructural evolution of the film using post-mortem atom probe tomography and transmission electron microscopy characterization. The results of which address how segregating behavior can be used as a means of thin film stress engineering.

5:00pm **TF+AS+NS+SA-ThA9 Development of an Analytical Model for Langmuir-Blodgett Silica Microsphere Assembly and Investigation of Ge Back Filling of the Opal Template by Polymer-Assisted Deposition**, ***Sarun Atiganyanun***, *M. Zhou, S.E. Han, S.M. Han*, University of New Mexico

Self-assembled photonic crystals find a wide variety of applications, including low-loss waveguides, high-efficiency solar cells, and thermal emission control. Here, we investigate a low-cost scalable fabrication of an opal structure via self-assembly of colloidal silica microspheres and propose a model describing a relationship between assembly parameters. To fabricate an opal structure, silica microspheres with a diameter of ~900 nm are first functionalized with allyltrimethoxysilane. Langmuir-Blodgett (LB) method is then used to self-assemble silica microspheres onto Si(100) substrates. By optimally adjusting the pulling speed of the substrate and surface pressure within the trough, a hexagonally closed-packed structure is achieved. By repeating LB coating processes for *n* number of times, an *n*-multilayer assembly is formed, creating an opal template structure. Scanning electron microscopy and light diffraction experiment are used to identify assembly parameters that give the largest domain size. An analytical model is also derived from material flux balance and a 2D van der Waals equation of state of silica spheres on water surface to describe the relationship between pulling speed, surface pressure, barrier speed, number of layers, and sphere's diameter for optimal assembly. In this presentation, we will also discuss a facile approach to back-fill opal templates via polymer-assisted deposition of Ge. After forming the template structure, a solution of polyethylenimine, ethylenediaminetetraacetic acid and germanium dioxide is used to back-fill the voids between microspheres. The sample is then annealed in a forming gas environment, forming Ge films around the microspheres. After the microspheres are removed, the Ge structure is characterized with SEM, XRD, and light transmission.

5:20pm **TF+AS+NS+SA-ThA10 The Determination of Porosity and Pore Size Distribution of The Al_2O_3 Antireflection Coating Deposited By Atomic Layer Deposition**, ***Chao Li***, *M. Goorsky*, University of California at Los Angeles

The porosity and pore size distribution of coatings prepared by atomic layer deposition and by other deposition techniques is important to understand their optical and mechanical properties. Specular X-ray reflectivity (SXRR) is capable of extracting layer thickness with angstrom resolution as well as determining the layer density. This makes it a good candidate for the porosity characterization of the antireflection coatings. On the other hand, advances in the development of X-ray generators and optics have made in-house glancing incidence small angle X-ray scattering (GISAXS) experimentation suitable for thedetermination of the size and shape of pores (in the scale of sub-nanometer to 100 nm) existing in thin films. It can be realized through the simulation of pore scattering based on distorted wave Born approximation (DWBA). Unfortunately, previous GISAXS studies failed to exclude the scattering from the rough surface and interfaces of thin films from the total scattering that was used for the simulation. In this study, we propose a refined GISAXS method characterizing the pore size distribution with the scattering from the rough surface and interfaces excluded. The scattering from the surface and interfaces was determined by the simulation of X-ray reflectivity (XRR) longitudinal scan with the parameters of the surface roughness σ, the lateral correlation length ξ and the Hurst parameter h extracted from the atomic force microscopy measurement, and layer thicknesses, densities and compositional grading determined by the specular XRR simulation. This refined GISAXS method, together the SXRR technique, was applied to utilized to reveal the effect of deposition techniques on the nanostructures of single-layer Al_2O_3 -based antireflection coatings. They were deposited using atomic layer deposition (ALD) which is a good candidate for multilayer antireflection coatings, due to the self-limiting nature of chemical reactions resulting in the precise control of film thickness and large-area uniformity. Each of them has two amorphous structures on a Si substrate grown with different deposition parameters. It is indicated by the refined GISAXS method that the first Al_2O_3 single layer is porous with a mean pore (spherical shape) radius of 7.2 nm while there are no pores in the second Al_2O_3 single layer. This agrees well with the SXRR showing a lower density of the first Al_2O_3 single layer (2.93 g/cm^3) than that of the second Al_2O_3 single layer (3.04 g/cm^3).

5:40pm **TF+AS+NS+SA-ThA11 Tuning Static and Dynamic Magnetic Properties of FeGa/NiFe Multilayer Composites**, ***Colin Rementer***, *Q. Xu, K. Fitzell, Z. Yao, P. Nordeen, G. Carman, Y. Wang, J.P. Chang*, University of California at Los Angeles

Traditionally, the use of magnetic materials in high frequency applications has been limited to oxides. This is because the materials' high resistivity, which reduces the formation of eddy currents by the incident electromagnetic waves. However, these oxides have limited applications in multiferroics, which are materials that possess more than one ferroic ordering in a single phase or strain-coupled composite systems, due to their low magnetomechanical coupling. Metallic materials are more desirable to this end, but their magnetic hardness and conductive losses have limited their use.

Rare-earth-free iron-gallium (FeGa) is one of the most promising magnetostrictive materials for use in composite multiferroics, due to its high piezomagnetic coefficient (3 ppm/Oe) and high stiffness (70 GPa). It has been integrated into several multiferroic systems, but generally in the MHz range or below[1]. This is due to the fact that the material has a large ferromagnetic resonance (FMR) linewidth (>300 Oe) at *X* band (9.6 GHz), which will result in incident energy being converted to heat. Metalloid dopants have been used to soften magnetic materials and to tune frequency dependent properties, such as permeability and piezomagnetic behavior, but at the cost of saturation magnetization as well as magnetostriction[2]. In this work, multilayer laminates containing alternating hard and soft ferromagnetic layers were fabricated to reduce loss at high frequencies.

FeGa (hard) and NiFe (soft) were sputtered via alloy targets into multilayers on Si [100] and piezoelectric substrates with total thicknesses ranging from 40-500 nm. The compositions of the films were verified via X-ray photoelectron spectroscopy (XPS) and were found to be Fe_yGa_{1-y} (78≤y≤85

at%) and Ni_xFe_{1-x} (79≤x≤83 at%). Static magnetic properties were evaluated via superconducting quantum interference device (SQUID) magnetometry, and it was found that the incorporation of NiFe layers was found to reduce the coercivity by up to 80%, while only reducing the saturation magnetization by 20%. FMR measurements revealed a narrowing of the linewidth by up to 90% at *X* band. Permeability extracted from the reflection coefficient (S11) obtained via stripline measurement was found to be affected by layer thickness and number of layers. FeGa showed strong magnetoelastic behavior and the multilayers are expected to exhibit an enhanced piezomagnetic effect due their reduced coercivity.

References:

1.M. Hamashima, C. Saito, M. Nakamura and H. Muro, Electr Commun Jpn 95 (5), 1-7 (2012).

2.J. Lou, R. E. Insignares, Z. Cai, K. S. Ziemer, M. Liu and N. X. Sun, Appl Phys Lett 91 (18) (2007).

Authors Index

Bold page numbers indicate the presenter

— A —

Alling, B.: TF+AS+NS+SA-ThA1, 1
Atiganyanun, S.: TF+AS+NS+SA-ThA9, **2**
Ayers, J.E.: TF+AS+NS+SA-ThA6, 2

— B —

Batra, V.: TF+AS+NS+SA-ThA3, **1**

— C —

Carman, G.: TF+AS+NS+SA-ThA11, 2
Chang, J.P.: TF+AS+NS+SA-ThA11, 2
Conley, J.F.: TF+AS+NS+SA-ThA2, 1

— F —

Fitzell, K.: TF+AS+NS+SA-ThA11, 2

— G —

Gall, D.: TF+AS+NS+SA-ThA4, 1
Goorsky, M.: TF+AS+NS+SA-ThA10, 2
Greene, J.E.: TF+AS+NS+SA-ThA1, 1

— H —

Han, S.E.: TF+AS+NS+SA-ThA9, 2
Han, S.M.: TF+AS+NS+SA-ThA9, 2
Harshan, V.N.: TF+AS+NS+SA-ThA3, 1
Hellman, O.: TF+AS+NS+SA-ThA1, 1
Huang, Y.: TF+AS+NS+SA-ThA2, 1
Hultman, L.: TF+AS+NS+SA-ThA1, 1

— K —

Kaub, T.: TF+AS+NS+SA-ThA8, 2
Keszler, D.: TF+AS+NS+SA-ThA2, 1
Kotru, S.: TF+AS+NS+SA-ThA3, 1
Kujofsa, T.: TF+AS+NS+SA-ThA6, **2**

— L —

Li, C.: TF+AS+NS+SA-ThA10, **2**

— M —

Mansergh, R.H.: TF+AS+NS+SA-ThA2, 1
Martens, R.L.: TF+AS+NS+SA-ThA8, 2
Mei, A.B.: TF+AS+NS+SA-ThA1, **1**
Murari, N.: TF+AS+NS+SA-ThA2, **1**

— N —

Nordeen, P.: TF+AS+NS+SA-ThA11, 2

— P —

Petrov, I.: TF+AS+NS+SA-ThA1, 1

— R —

Ramana, C.V.: TF+AS+NS+SA-ThA3, 1
Rementer, C.: TF+AS+NS+SA-ThA11, **2**
Rockett, A.: TF+AS+NS+SA-ThA1, 1

— S —

Sangiovanni, D.G.: TF+AS+NS+SA-ThA1, 1
Schlepütz, C.M.: TF+AS+NS+SA-ThA1, 1

— T —

Thompson, G.B.: TF+AS+NS+SA-ThA8, 2

— V —

Varagas, M.: TF+AS+NS+SA-ThA3, 1

— W —

Wang, Y.: TF+AS+NS+SA-ThA11, 2
Westerfield, G.: TF+AS+NS+SA-ThA2, 1
Wireklint, N.: TF+AS+NS+SA-ThA1, 1

— X —

Xu, Q.: TF+AS+NS+SA-ThA11, 2

— Y —

Yao, Z.: TF+AS+NS+SA-ThA11, 2

— Z —

Zheng, P.Y.: TF+AS+NS+SA-ThA4, **1**
Zhou, M.: TF+AS+NS+SA-ThA9, 2
Zhou, X.: TF+AS+NS+SA-ThA8, **2**