Thin Film
Room: 302 - Session TF-ThM

Evaporation, Pulsed Laser Deposition, and Molecular Beam Epitaxy

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

8:00am **TF-ThM1 Pulsed Laser Dewetting of Patterned Thin Metal Films: A Means of Directed Assembly**, ***Y.F. Guan***, The University of Tennessee, Knoxville, *J.D. Fowlkes, A.V. Melechko, M.L. Simpson,* Oak Ridge National Laboratory, *P.D. Rack*, The University of Tennessee, Knoxville

One of the challenges of nanoscience and technology is understanding and controlling bottom up directed assembly of materials. A lot of work has been done studying the assembly of continuous thin polymer and metal films which reveal interesting dewetting phenomenon. While the break-up and pattern formation via dewetting of continuous thin metal and polymer films has been studied in detail, less work has been devoted to the dewetting and pattern formation of confined or patterned thin films. In this work, thin nickel films were patterned into various shapes and treated via nanosecond pulsed laser processing. The short liquid lifetimes offers a unique way to monitor the time dependence of the dewetting process and the subsequent pattern formation. Thin nickel films (30 nm) were evaporated onto electron beam lithography patterned PMMA coated (60 nm) silicon substrates. Thin nickel patterns of a variety of sizes of circles, squares, and triangles were achieved by a conventional lift-off process. The edges and vertices of the patterned shapes act as programmable instabilities which enable directed assembly via dewetting when the laser energy density is above the melting threshold. The pattern formations were monitored as a function of laser pulse and the retraction process was attributed liquid dewetting and a subsequent re-solidification. The calculated retraction velocity (83 m/s) and liquid lifetime (12.3 ns) were consistent with the measured nickel retraction distances. The lateral retraction and pattern formation was correlated to a two step process: 1) initially the surface tension drives the flow of the melted nickel films, and 2) a smaller contraction associated with the density difference between the liquid and solid when the liquid film solidifies. The vertices of the shapes had an initially larger retraction velocity which was attributed to an additional in-plane curvature. The reduced retraction rates at subsequent pulses were attributed to thickening of the front which reduces the curvature and enhances viscous dissipation. Acknowledgements: The authors acknowledge support from the Material Sciences and Engineering Division Program of the DOE Office of Science. And a portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

8:20am **TF-ThM2 Vacancy Ordered Screw Form (VOSF) and Layered Indium Selenide (In_2Se_3) Thin Films by Pulsed Laser Deposition**, ***E. Venkatasubramanian***, *F.S. Ohuchi,* University of Washington, *P. Nachimuthu, K.M. Beck*, Pacific Northwest National Laboratory

Indium Selenide (In_2Se_3) is an interesting material in the Chalcogenide family and has long been studied owing to its applications in Photovoltaics, optical waveguides and as battery material among others. It has recently garnered even more attention since being demonstrated as a viable phase change memory material with properties that could better GST. Device applications such as these require a film growth technique that is fast, has a high throughput along with the ability to make the desired composition relatively easily. Pulsed Laser deposition is one method that meets all the above criteria and it has also been widely used for making combinatorial samples and thus any optimization study could be done faster. In this work, we report the thin film growth of In_2Se_3 by Pulsed laser deposition. Here film deposition was carried out using a 355 nm Nd:YAG laser with a short 5ns pulse width, operating at 20 Hz. Films were subsequently characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Scanning electron microscopy. Both single-phase VOSF and layered In_2Se_3 have been obtained exclusively by controlling the deposition conditions and post deposition in-vacuo annealing. The deposited films were found to be uniform and highly oriented along the c-axis. Film stoichiometry and thickness were evaluated by Rutherford Back Scattering and are in accordance with the formula unit and compare well with those obtained from vapor deposited films. Out of plane conductivity measurements were carried out with films deposited on TiN/Si and showed a large difference in conductivity between the amorphous and VOSF phases thereby supporting the use of PLD for growing thin films for Phase Change memory device applications.

8:40am **TF-ThM3 Electrical Conductivity and Thermopower of Ti_nO_{2n-1} Thin Films grown by Pulsed Laser Deposition**, ***N. Nguyen***, University of Washington, *A. Yamamoto,* Advanced Industrial Science and Technology Institute, Japan, *T. Chikyow,* National Institute for Materials Science, Japan, *F.S. Ohuchi*, University of Washington

Reduced titanium dioxide (TiO_2) in thin film forms are investigated as a new class of oxide materials for thermoelectric applications. Deposition of thin films was carried out at temperature of 800 °C and oxygen partial pressure of 10^{-7} torr on both $SrTiO_3$ (001) and $LaAlO_3$ (001) substrates by pulsed laser deposition (PLD). Initial X-ray diffraction characterizations indicate that thin films are crystallized into a mixture of polycrystalline and texture Magneli phases, Ti_nO_{2n-1} where n = 4, 5, 6… Electrical conductivity (Σ) and Thermopower (S) of the samples were measured over a temperature range from 10 K to 500 K, from which power factors ($S^2\sigma$) were evaluated as a function of temperature. It was found that Ti_nO_{2n-1} thin films deposited on $SrTiO_3$ yielded unusually large power factors, at room temperature and bellow. These values were at least several times larger than those found on Ti_nO_{2n-1} films deposited on $LaAlO_3$ and typical bulk thermoelectric materials such as $Na_xCo_2O_4$ and Bi_2Te_3 at room temperature, and by an order magnitude around T~100K. In addition, the thermopower from thin films deposited on $SrTiO_3$ exhibits large deviation from a small polaron hopping transport mechanism, suggesting that interface defects in a form of oxygen vacancies introduced during PLD play an important role in thermoelectric transport process.

9:00am **TF-ThM4 Effects of Pulsed Laser Deposition Conditions on the Growth of Ge Quantum Dot on Si(100)-(2x1)**, ***A. Er***, *H. Elsayed-Ali*, Old Dominion University

The growth of Ge quantum dots (QD) by pulsed laser deposition of Ge on Si(100)-(2x1) is studied. The samples were first cleaned by using modified Shiraki and IMEC methods and then transferred into the deposition chamber. The vacuum system was then pumped down, baked for at least 12 hours, and the sample was then flashed to 1100 °C in order for the 2´1 reconstruction to form. The experiment was conducted under a pressure ~1x10-9 torr. A Q-switched Nd:YAG laser (wavelength l = 1064 nm) with 10 Hz repetition rate was used to ablate a Ge target. Different substrate temperatures and ablation laser energy densities were used and were shown to affect the quantum dot morphology. In-situ RHEED and ex-situ STM and AFM were used to study the morphology of the grown QD. During deposition, the RHEED patterns changed from elongated streaks to spots. As we increased the ablation laser energy density or the substrate temperature, formation of RHEED spots occurred at less coverage. AFM scans show that the number of clusters and coverage ratio increases with the ablation laser energy density, while the average area of clusters decreases. As we increased the substrate temperature from 400±20 to 500±20 oC, the Ge QD morphology changed from the asymmetric hut shape to the symmetric dome shape. Also, a decrease in the number of clusters and coverage ratio was observed.

9:20am **TF-ThM5 Unique Initial Growth Mode for Rare-Earth Group-V Nanocrystals on III-V Semiconductors**, ***S.G. Choi***, *Y. Yan,* National Renewable Energy Laboratory, *B.D. Schultz,* International Technology Center, *C.J. Palmstrom*, University of California, Santa Barbara

Incorporation of rare-earth group-V (RE-V) compounds into III-V semiconductors has generated considerable interests as a result of their potential applications in thermodynamically stable metallic contacts to III-V semiconductors and metal-based novel electronic devices. It has recently been demonstrated that RE-V's in a nanocrystal (NC) form embedded in III-V semiconductor matrix can extend their applications to advanced photonic devices and high-efficiency thermoelectric devices.[1,2] High device performance relies upon the synthesis of heterostructures in a controlled manner, and therefore a good understanding of the structure for the growth front is of great importance. Even though early growth studies have shown that the formation of RE-V's on III-V semiconductors is not associated with any of the typical growth modes, details of their unique growth nature were not discussed until recently.[3,4] Our in-situ surface studies on ErAs/GaAs[3] and ErSb/GaSb[4] systems suggest that the incoming Er atoms displace the Ga atoms in the substrate and form ErAs and ErSb nanocrystals "within" the substrate surface rather than on top. After 3 – 4 monolayers deposition, RE-V NCs form a continuous layer and then grow via "layer-by-layer" modes for the remaining growth. We have used cross-sectional high-resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) to study the ErSb NC formation as a result of

1 monolayer ErSb deposition on molecular beam epitaxially grown GaSb(001) surfaces. The HAADF-STEM studies clearly show the formation of ErSb NCs "within" the GaSb substrate surface consistent with the in-situ surface science studies and the embedded growth model.[3,4] In this presentation, we will correlate ex-situ cross-sectional HAADF-STEM results with in-situ reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoemission spectroscopy, and scanning tunneling microscopy studies to determine the unique formation mechanism involved during the growth of ErAs and ErSb NCs in III-V semiconductors. This work was supported in part by ARO and NSF-MRSEC. This abstract is subject to government rights.

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9:40am **TF-ThM6 Growth and Characterization of Cuprous Oxide Nanoclusters on Strontium Titanate (100) Surface**, ***S.V.N.T. Kuchibhatla***, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *S. Thevuthasan, P. Nachimuthu, V. Shutthanandan, C.M. Wang, Y. Li, C.H. Henager, Jr., S.K. Sundaram*, Pacific Northwest National Laboratory

Growth of electronic materials as single crystals for a variety of uses can be limited by the lack of fundamental understanding of the nucleation, growth, and coalescence regime at the initial stages of the growth process. As a first step in comprehensively developing a knowledge database on the nucleation and growth of various materials, we have investigated the growth of cuprous oxide (Cu_2O) nanoclusters on $SrTiO_3$(100) substrate. There has been considerable interest in Cu_2O nanoclusters because they can be used effectively in chemical and photochemical applications due to their unique electronic transport properties. We have grown Cu_2O clusters using oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and the effects of deposition rate, substrate temperature, oxygen pressure, and deposition time were systematically studied. Structural, morphological, and chemical properties of these clusters were investigated using several surface and bulk interrogation methods. X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) measurements clearly demonstrated the complex nature of the copper oxide system due to the possibility of co-existing Cu(0), Cu(1), and Cu(2) phases in the clusters. Optimum deposition conditions were established to produce pure Cu_2O clusters. Atomic force microscopy (AFM) images clearly showed the growth of uniformly distributed epitaxial, faceted pure Cu_2O clusters on STO (100) with (100) orientation. Rutherford backscattering spectrometry (RBS) measurements have been used along with the AFM and transmission electron microscopy (TEM) measurements to compute the thickness of the films. The cluster size, shape and their preferred orientation were critically analyzed. It is observed that the surface morphology, cluster coalescence, and film formation are highly dependent on various growth parameters including growth rate, deposition temperature, and deposition time. Theoretical investigations have also been carried out to understand growth mechanisms and these results will be presented along with the experimental observations.

10:40am **TF-ThM9 Low Temperature Growth of High-Quality Indium Nitride on Si(100) by Femtosecond Pulsed Laser Deposition**, ***M.A. Hafez***, *H. Elsayed-Ali*, Old Dominion University

The growth and structural properties of indium nitride (InN) grown on Si(100) substrates by femtosecond pulsed laser deposition (fsPLD) are studied. Deposition InN on Si(100) is performed with an amplified Ti:sapphire laser (130 fs) at wavelength of 800 nm. Laser induced gas breakdown-assisted PLD is used to generate reactive nitridation from ammonia. Prior to InN growth, an intermediate two-dimensional layers of indium on Si(100) surface at substrate temperature of ~70 ºC is performed by fsPLD under ultrahigh vacuum (low 10^{-9} Torr). In situ reflection high-energy electron diffraction (RHEED) is used during the deposition to monitor the structure and morphology of the film growth. The InN films are prepared at room temperature to a substrate temperature of ~350 ºC. The grown films are examined by ex situ atomic force microscopy, scanning electron microscopy, and x-ray diffraction (XRD). RHEED and XRD analysis showed high-quality InN films grown on Si(100). The quality and structural properties of the InN films are improved by employing a low-temperature buffer layer and by the nitridation process. RHEED observation showed that InN grew on Si(100)-(2x1) surface by the Stranski-Krastanov mode. The growth mode and morphology of the InN films is influenced by the surface condition of Si(100) substrate. The kinetic effect of the PLD has a main rule in improving the initial layers and the formation of InN. The obtained results demonstrate the potential of the growth procedure for deposition of high quality InN epitaxial layers by fsPLD at reduced temperatures.

11:00am **TF-ThM10 Thin Films by Metal-Organic Precursor Plasma Spray**, ***D.L. Schulz***, *R.A. Sailer*, North Dakota State University, *J. Leach, R. Molz*, Sulzer Metco (US)

While most plasma spray routes to coatings utilize solids as the precursor feedstock, metal-organic precursor plasma spray (MOPPS) is an area that we have investigated recently as a novel route to thin film materials. Very thin films are possible via MOPPS and the technology offers the possibility of forming graded structures by metering the liquid feed. To date, liquid-based precursor plasma spray efforts have utilized solutions of metal salts or dispersed colloidal particles with a limitation of these approaches related to the fact that most of the plasma energy is expended toward evaporation/combustion of the solvent which starves this process of the energy required to promote film formation. The current work employs metal-organic compounds that are liquids at standard temperature-pressure conditions. In addition, these complexes contain chemical functionality that allows straightforward thermolytic transformation to targeted phases of interest. Toward that end, aluminum sec-butoxide (Al(OBu)3) and aluminum 3,5-heptanedionate (Al(hd)3) were used as precursors to alumina while triethylsilane (HSi(C2H5)3) and titanium tetrakisdiethylamide (Ti(N(C2H5)2)4) were employed for studies toward silicon carbide and titanium-nitride-carbide. In all instances, the precursors contain metal-heteroatom bonds envisioned to provide atomic concentrations of the appropriate reagents at the film growth surface thus promoting phase formation (e.g., Si-C bond in triethylsilane, Ti-N bond in titanium amide, etc.). Films were deposited using a Sulzer Metco Triplex Pro-200 Plasma Spray system under various experimental conditions using Design of Experiment (DoE) principles. The composition and morphology of these films was studied as a function of application conditions. Film compositions were analyzed by glancing incidence x-ray diffraction (GXRD) and elemental determination by x-ray spectroscopy (EDS). Silicon carbide and titanium-nitride-carbide films typically exhibited a continuous morphology with reasonable adhesion (i.e., passed tape pull adhesion test) while aluminum oxide films ranged from powdery to continuous but suffered from poor adhesion.

11:20am **TF-ThM11 Dependence of Fiber Texture on Composition in Au-SiO_2 Composite Thin Films**, ***D.I. Filoti***, *A.M. Brown, D. Carlson, J.M.E. Harper*, University of New Hampshire

We show that the evolution of metal fiber texture in sputtered metal-insulator composite thin films depends strongly on the composition through the presence of second-phase particles that interrupt normal metal grain growth. Using x-ray diffraction pole figures, we measured the strength of the Au(111) fiber texture as a function of composition in the Au-SiO_2 system, which phase segregates during deposition. For very low SiO_2 volume fractions less than 0.05, the Au has low resistivity and a strong (111) fiber texture similar to that of pure Au. For higher SiO_2 volume fractions up to 0.3, the strength of the fiber texture decreases rapidly with increasing volume fraction of SiO_2 second-phase particles, and the resistivity increases. For SiO_2 volume fractions greater than 0.3, the fiber texture is lost as the Au becomes discontinuous and the microstructure changes to randomly oriented Au islands within an insulating matrix of SiO_2, confirmed by resistivity and transmission electron microscopy measurements. We show that the rapid decrease in Au(111) fiber texture strength correlates with a reduction in Au grain size caused by Zener pinning of Au grains by second-phase SiO_2 particles. Grain boundary pinning by second-phase particles prevents the development of (111) fiber texture that usually occurs during normal grain growth. The result is a more rapid loss of fiber texture as a function of composition than can be explained only by the decreasing Au volume fraction.

11:40am **TF-ThM12 Phase Transformation Behaviors of SiO_2 Doped $Ge_2Sb_2Te_5$ Films for Application in Phase Change Random Access Memory**, ***S.W. Ryu***, *J.H. Lee, Y.B. Ahn, C.S. Hwang, H.J. Kim*, Seoul National University, South Korea

Phase change random access memory (PCRAM) has attracted a great interest because it satisfies various demands for nonvolatile memory devices.[1-3] PCRAM uses the reversible phase change between the crystalline and amorphous states of chalcogenide materials, such as $Ge_2Sb_2Te_5$ (GST), brought about by Joule heating. However, the high level of I_{res} has been the major obstacle to the further scaling of PCRAM because of the limited on-current drive capability of the cell transistor (<0.5 mA/μmm). There have been several reports on the improvement of the switching performance of GST achieved by doping it with various impurities, such as N,[4] O,[5] Si,[6] or SiO_2.[7] In the case of SiO_2 doped GST (S-GST), it was reported that the reset current is reduced by approximately 50% compared to that of undoped GST. [12] The improvement in the phase change characteristics of GST films was investigated by doping the GST films with SiO_2 using cosputtering at room temperature. As the sputtering power of SiO_2 increased from 0 to 150 W, the activation energy for crystallization increased from 2.1±0.2 to 3.1±0.15 eV. SiO_2 inhibited the crystallization of the amorphous GST films,

which improved the long term stability of the amorphous phase. The melting point decreased with increasing concentration of SiO_2,which reduced the power consumption as well as the reset current.

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