

## Thin Film

Room: Ruidoso - Session TF+EM-MoM

## Nanostructuring Thin Films

Moderator: A. Melechko, North Carolina State University

8:20am **TF+EM-MoM1 Nanostructured Magnetic Thin Film Heterostructures: Fabrication, Exchange Interactions and Tailored Anisotropies**, *K.M. Krishnan*, University of Washington **INVITED**

Ultrathin metallic heterostructures show richness in magnetic behavior driven, in part, by exchange, interface, proximity, size and dimensionality effects. One of the most widely studied and technologically important, but still not well-understood, magnetic behavior is the phenomenon of exchange bias (EB) observed in ferromagnetic (FM)/antiferromagnetic (AFM) structures. In this talk, I will first discuss epitaxial growth of such MnPd/Fe bilayers with tailored AFM spin-lattices (compensated and uncompensated) at the interface exhibiting in-plane EB and  $(\text{Co}_{x-1}\text{Pt}_y\text{Al})_n/\text{IrMn}$  multilayers with perpendicular EB. Asymmetric magnetization reversals in *exchange*-biased Fe/MnPd bilayers were confirmed by photoemission electron microscopy (PEEM) with x-ray magnetic circular dichroism (XMCD) for magnetic contrast. Further, the element-specific magnetic structure of the  $\text{Mn}_{52}\text{Pd}_{48}/\text{Fe}$  bilayer was investigated with atomic-layer depth sensitivity at the antiferromagnet/ferromagnet interface by soft-XMCD and magnetic reflectivity (XMR). A complex magnetic interfacial configuration, consisting of a 2-monolayer-thick induced ferromagnetic region, and pinned uncompensated Mn moments that reach far deeper ( $\sim 13$  Å), both in the antiferromagnet, were found. These epitaxial EB samples also show in-plane reorientation transitions, determined by the competition between the interface exchange coupling and the intrinsic uniaxial energies, and is driven by the temperature, as well as the thickness of MnPd and Fe layers. Complementing these results, work on multilayers show that perpendicular EB arise from a complex interplay between unidirectional anisotropy at the terminating FM/AFM interface, the perpendicular anisotropy of the FM/nonmagnet (NM) multilayer stack and the overall magnetostatic energy of the structure. Finally, we have developed and implemented nanoimprint lithography (NIL) to fabricate wire and particle arrays of exchange biased elements at the 300nm length scale. A mask transfer NIL process has also been developed to grow epitaxial structures. The role of size and dimensionality as well as competing anisotropies, introduced by particle shape, on EB heterostructured elements has been studied. Details will be presented.

9:00am **TF+EM-MoM3 Self and Directed Assembly of Thin Metallic Films by Pulsed Laser Induced Dewetting**, *Y. Wu*, University of Tennessee, *J.D. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee

The synthesis and assembly of functional metallic nanomaterials is critical for realizing many important applications of nanoscience and nanotechnology. In this study, we investigated thin film dewetting of metal films via pulsed nanosecond laser melting. We studied film instabilities induced by capillary forces and the subsequent mass transport which can lead to thin film break-up and subsequent nanoparticle formation. We have also explored the dewetting and nanopattern formation of nano-lithographically patterned thin films of various shapes to understand how various initial and boundary conditions can guide the assembly. In this presentation we will discuss the various spinodal and Rayleigh-Plateau instability mechanisms and the inertial, visco-inertial and viscous flow regimes involved in the thin metal film assembly. Finally we will discuss how nano-lithographically defined features can be used to direct the assembly of multi-functional nanoparticle ensembles.

9:20am **TF+EM-MoM4 Plasma-assisted Metallorganic Chemical Vapor Deposition of ZnO Nanostructures: Impact of Process Parameters on Dimensionality and Morphology**, *M. Bonvalot*, *G.M. Rosaz*, Ltm-Cnrs, Cea-Leti, France

ZnO is a II-VI semiconductor with a large band gap (3.4 eV) and excitonic binding energy (60 meV), which make it particularly attractive for a great diversity of potential emerging applications in the field of nanotechnologies (UV light emitters, laser diodes...). Several synthesis routes of ZnO nanostructure arrays have been reported in the literature, essentially on sapphire substrates. However, very few studies have been reported on growth of ZnO nanostructures on Si(111) substrates due to the difficulty of matching materials with different spatial symmetry group.

In this study, ZnO nanostructures have been prepared on Si(111) by plasma assisted pulsed injection MOCVD (metallorganic chemical vapor deposition). This technique of elaboration offers the advantage of large area growth and is compatible with existing semiconductor processing technologies. The key role of the plasma during material preparation is to allow lower substrate temperature (as low as 350°C), thus providing lower activation energies. It also allows in situ thermal treatment of substrates and prepared nanostructures. Moreover, the active chemical species of the plasma can help force in situ doping of the semiconducting nanostructure, which opens up a large spectrum of metastable phase formation possibilities.

We have investigated the effect of several process parameters (precursor flow rate, O<sub>2</sub>/Ar partial pressure, plasma incident power) on the morphology of the produced nanostructures. Three growth regimes have been identified: 2 dimensional very fine grain thin films, ordered hexagonal shaped plates and oriented columnar grains with a very large density corresponding to nanowire growth. These results will be presented in the light of literature data [1, 2]. The transition between these three different growth regimes is induced by a careful adjustment of the substrate temperature and Ar/O<sub>2</sub> plasma flowrate. The role of these process parameters will be highlighted based on gas phase OES and SEM analyses, and the growth mechanism of densely packed 1D ZnO nanostructures will be presented.

[1] S. Agouram, J.A. Bastos-Segura and V. Munoz-Sanjos, <http://www.sciencedirect.com/science/journal/07496036> **42**, 140 (2007).

[2] J. B. Baxter and E. S. Aydil, *J. Electrochem. Soc.* **156** (1) H52-H58 (2009).

9:40am **TF+EM-MoM5 Self-assembled and Engineered Nanostructures in  $\text{Hf}_{1-x}\text{Al}_x\text{N}/\text{MgO}(001)$  Single-Crystal Alloys: Effects on Physical Properties**, *B. Howe*, *E. Sammann*, *J.-G. Wen*, *M. Sardela*, *T. Spila*, *J. Greene*, University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden, *I. Petrov*, University of Illinois at Urbana-Champaign

Transition metal nitrides (TMN) are well known to have a remarkable range of unique physical properties. One method used to further enhance the physical properties of many transition metal nitrides is to alloy them with a second, thermodynamically immiscible nitride. The most famous example is  $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ; many have reported drastically enhanced physical properties including super hardness, increased oxidation resistance, age-hardening behavior, and the formation nanoscale compositional modulations during film growth and post annealing experiments. However, very little has been reported on the ability to control this nanostructure, nor has the effect of these nanostructures on the physical properties of the films. We have chosen  $\text{Hf}_{1-x}\text{Al}_x\text{N}$  as a model system to study the nanostructures of interest. We begin by reporting on the effects of nanostructure on the optoelectronic, thermal transport and elastic constant properties of  $\text{Hf}_{1-x}\text{Al}_x\text{N}$  single crystal layers grown on  $\text{MgO}(001)$  using ellipsometry, temperature dependent hall effect, and picosecond probe acoustic transport measurements, respectively. We continue by summarizing a systematic study into the effects of growth parameters (ion energy,  $E_i$ , ion-to-metal flux ratio,  $J_{\text{ion}}/J_{\text{me}}$ , and substrate temperature,  $T_s$ ) on single crystal reactively sputtered  $\text{Hf}_{0.7}\text{Al}_{0.3}\text{N}/\text{MgO}(001)$  layers in order to controllably manipulate the nanostructure and study its effects on the physical properties. Films are deposited from a Hf/Al 70/30 (at. %) target in 5% N<sub>2</sub>/Ar mixtures while  $J_{\text{ion}}/J_{\text{me}}$  is varied from 0.7 to 12.6,  $T_s$  from 400 to 700 °C, and  $E_i$  from 10 to 80 eV.  $J_{\text{ion}}/J_{\text{me}}$  has a strong effect on the formation of 3D nanoscale (2-3nm) compositional modulations as indicated by HR-XRD and HR-TEM. Nanoindentation experiments reveal an increase in film hardness from 31.7 ± 0.6 GPa to 38.9 ± 0.6 GPa.  $E_i$  has a strong effect on the AlN incorporation probability, which can be adjusted between ~ 0 and 100% by varying the ion energy ( $E_i$ ) incident at the growing film over a narrow range, 10-40 eV. Epitaxial film compositions vary from  $x = 0.30$  with  $E_i = 10$  eV, to 0.27 with  $E_i = 20$  eV, 0.17 with  $E_i = 30$  eV, and ≤ 0.002 with  $E_i \geq 40$  eV. This extraordinary range in real-time manipulation of film chemistry during deposition is due to the efficient resputtering of Al atoms (27 amu) by Ar<sup>+</sup> ions (40 amu) backscattered from Hf atoms (178.5 amu). We demonstrate that this effect can be used to grow superlattices with abrupt interfaces at high deposition rates from a single target by switching  $E_i$ . We grew superlattices with bilayer thicknesses from 1-6nm and films exhibited an increase in hardness from 32.5 ± 0.9 GPa to 37.8 ± 1.2 GPa.

10:00am **TF+EM-MoM6 Lowering the Epitaxial Growth Temperature of Ge Quantum Dots on Si(100)-(2x1) by Electronic Excitation**, A.O. Er, H. Elsayed-Ali, Old Dominion University

Low temperature epitaxy is important for device fabrication because it can lead to suppressing the introduction of defects such as dislocations and stacking faults. The effect of laser-induced electronic excitations on the self-assembly of Ge quantum dots (QDs) on Si(100)-(2x1) grown by pulsed laser deposition is studied. The experiment was conducted in ultrahigh vacuum. A Q-switched Nd:YAG laser (wavelength  $\lambda = 1064$  nm, 10 Hz repetition rate) was split into two beams; one used to ablate a Ge target while the other to electronically excite the substrate. In-situ reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM), and ex-situ atomic force microscopy (AFM) were used to study the morphology of the grown QDs. The dependence of the QD morphology on substrate temperature and ablation and excitation laser energy density was studied. Electronic excitation is shown to affect the surface morphology. For Ge coverage of 22 monolayer, it was observed that excitation laser reduces the epitaxial growth temperature to 250 °C. Applying excitation laser to the substrate during the growth changes the QD morphology and island density and improves the size uniformity of QDs at 390 °C. Applying the excitation laser during growth decreases the surface roughness at room temperature. RHEED recovery curves show that applying excitation laser increases the surface diffusion. A purely electronic mechanism of enhanced surface diffusion of the Ge adatoms due to a phonon-kick mechanism following two-hole localization could explain the results. Ongoing experiments using a femtosecond laser for excitation and in-situ STM for detection of the early stages of island nucleation will be presented.

10:40am **TF+EM-MoM8 Novel Nanoparticle and Thin film Growth Via Matrix Assisted Pulsed Laser Evaporation of Metal Based Acetates**, M.A. Steiner, J.M. Fitz-Gerald, University of Virginia

Until recently, the majority of research surrounding Matrix Assisted Pulsed Laser Evaporation (MAPLE) has been concentrated on preserving the structure and properties of polymeric and biomaterials. Deviating from this course, novel research will be presented illustrating the feasibility of applying matrix-assisted processing to grow inorganic materials from precursor solutions in the form of complex nanoparticles and thin films. By replacing the preferentially absorbing matrix material with a transmitting solvent, laser energy is instead absorbed by a precursor solute which decomposes and is subsequently ejected onto the substrate in the form of nanoparticles. [1] [2] Acetates are a widely favored metallorganic precursor for thin film processing on various substrates because they decompose under ultraviolet irradiation. Results will be presented in the form of thin films and nanoparticle systems of Au-Ag-Pd, ZnO, and YBaCuO material systems.

[1] Allmond, C., Sellinger, A., Gogick, K., & Fitz-Gerald, J. (2007). Photochemical synthesis and deposition of noble metal nanoparticles. *Applied Physics A: Materials Science & Processing*, 86(4), 477-480

[2] Sellinger, A., Aburada, T., & Fitz-Gerald, J. (2008). Synthesis of multimetallic nanoparticles using a solution-based pulsed laser deposition approach. In *Proceedings of SPIE* (Vol. 7005, p. 700516)

11:00am **TF+EM-MoM9 Nanocomposite Vanadium Oxide Thin Films**, B.D. Gauntt, M.W. Horn, O.M. Cabarcos, E.C. Dickey, Penn State University

Thin film vanadium oxide is used as the active layer in un-cooled, infrared imaging devices based on microbolometer structures. In this type of imaging device, infrared radiation is detected via a temperature driven resistivity change in the active layer. Underlying readout circuitry and the need for increased detection sensitivity require low electrical resistivity material with high thermal coefficient of resistivity (TCR). Vanadium oxide thin films deposited via reactive pulsed direct current (DC) sputtering have properties in the range of interest with room temperature resistivity varying from 0.01 to  $6 \times 10^4$  Ohm cm and TCR's varying from -0.1 to -4.2 %/°C. Films with resistivity in the range of interest (0.1 to 1.0 Ohm cm) contain the rocksalt structured FCC  $\text{VO}_x$  phase ( $0.8 < x < 1.3$ ) accompanied by significant structural disorder, while those with greater resistivity are amorphous. The relationship between TCR and room temperature resistivity is exponential, and throughout the present series of films is fixed, i.e. a film with a given resistivity has a set TCR. Energy filtered electron diffraction patterns collected in the transmission electron microscope (TEM) reveal a diffuse scattering feature at low scattering angle for both amorphous and nanocrystalline films, suggesting that films containing nanocrystals also contain an amorphous phase. Raman spectroscopy results from amorphous films show a broad feature around  $\sim 890$   $\text{cm}^{-1}$ , while spectra from nanocrystalline films exhibit the "amorphous" feature and a second broad feature at  $\sim 300$   $\text{cm}^{-1}$ . The feature at  $\sim 300$   $\text{cm}^{-1}$  was the only feature present in the most crystalline of the films, suggesting it represents the disordered

FCC  $\text{VO}_x$  phase. Film stoichiometry, as measured with Rutherford backscattering spectroscopy, puts the overall chemistry of the nanocrystalline films outside the FCC  $\text{VO}_x$  phase field, with many of the samples having a V:O ratio greater than 1.3. A pre-peak feature in the V-K edge was observed with X-ray absorption spectroscopy (XAS), and the intensity of the pre-peak, which is known to result from local octahedral disorder, increased with increasing oxygen content and correlates with diffraction observations of increasing disorder. The combined TEM, RBS, Raman, and XAS analyses suggest vanadium oxide films with properties in the range of interest for microbolometer-based devices consist of a two-phase material containing FCC  $\text{VO}_x$  nanocrystals embedded in an oxygen-rich amorphous matrix. Films lacking sufficient disorder have resistivity in the range of interest but insufficient TCR magnitude, suggesting the need for both the nano-crystalline phase and the amorphous matrix.

11:20am **TF+EM-MoM10 Titanium-doped Carbon-based Nanocomposite Coatings, Mechanical and Tribological Properties, Biocompatibility and Cell-Attachment Properties: Implications in Orthopedic Implants**, P. Epaminonda, University of Cyprus, Y. Christou, A. Odysseos, EPOS-IASIS R&D, Cyprus, C. Rebholz, C. Tsotsos, University of Cyprus

Stress shielding due to uneven load distributions at the bone-prosthesis interface affect joint prostheses and can lead to wear and loosening. Commonly used cobalt-chromium-molybdenum alloys can degrade during wear at an average rate of 0.02–0.06 mm/year. Other alloys such as titanium-aluminium-vanadium although biocompatible and highly corrosion resistant, exhibit relatively low mechanical properties and poor wear resistance. Nanocomposite nanocrystalline (nc-) Ti(N,C)/ amorphous diamond-like-carbon (a-C:H) coatings exhibit high hardness (H), low friction coefficients, high wear resistance and resilience to substrate deformation thus making them promising candidates for prosthetic implant applications. In this work we investigate the influence of the microstructure of nc-Ti(N,C)/a-C:H coatings on the mechanical, tribological and biological properties with the aim of using such materials not only as wear resistant films in biomedical implants, but also as a bioactive surface that can promote bone ingrowth at areas of medical implants, such as the femoral stem or the acetabular cell in hip replacement joints, that are in direct contact with bone. Approximately 2  $\mu\text{m}$  thick, nc-Ti(N,C)/ a-C:H coatings were deposited on Si wafer and implant alloy coupons using low temperature ( $\sim 200$  °C) DC reactive magnetron sputtering. The carbon content was varied from 41 to 57 at % and the obtained a-C:H phase ranged from 31 – 47 at. % in order to form the desired nanocomposite structure of 2-4 nm wide Ti(N,C) with 1 to 2 monolayer coverage of a-C:H. An increase in the amorphous phase results in a decrease in mechanical and a decline in tribological performance, however the change in structure and surface morphology at increased carbon content favours the bioactivity of the films. Coating chemical composition and microstructure was investigated by means of x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and transmission electron microscopy (TEM). The mechanical and tribological properties of the films were determined using nanoindentation and nanotribo-scope methods. In order to assess the biocompatibility of nc-Ti(N,C)/a-C:H coatings and investigate their osteoblast - attachment properties and thus determine their efficacy as implant coatings, the osteoblastogenic osteosarcoma immortalised cell lines Saos-2 and Hos were seeded and allowed to grow on the coating surface. Cell attachment properties were assessed in terms of viability of seeded cells. Viable attached cells were quantified by a mitochondrial enzymatic activity-based colorimetric assay against cultures seeded on conventional tissue-culture treated plastic surface.

11:40am **TF+EM-MoM11 Magnetic Responsive Polymer Nanocomposites Thin Films: Synthesis, Characterization and Implementation in RF/Microwave Applications**, C. Morales, J. Dewdney, S. Skidmore, S. Pal, K. Stojak, H. Srikanth, T. Weller, J. Wang, University of South Florida

Newly-developed magnetic responsive polymer nanocomposites were elaborated using low complexity equipments and low-cost lab materials and apparatus. Sub-10nm  $\text{CoFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  nanoparticles with tightly controlled size distribution were synthesized using a chemical co-precipitation procedure, which involves Iron and Cobalt salts and oleic acid and oleylamine as surfactants. This polymer nanocomposite is dissolved in hexane together with calculated amount of surfactant-coated nanoparticles to obtain the polymer nanocomposites with uniform nanoparticle dispersion at desired concentration. Excellent dispersion of magnetic nanoparticles in the polymer matrix is very important for a low-loss material at microwave and RF frequencies, as it minimizes magnetic hysteresis losses by reducing magnetic coupling amongst particles. The amount and composition of all the constituent solvents is critically-controlled for the purpose of maintaining the desired viscosity to control the exact thickness of the thin film after solvent evaporation and the curing process.

The electrical microwave properties of Fe<sub>3</sub>O<sub>4</sub>-based polymer nanocomposites (e.g., permeability, permittivity and loss tangent) were tuned under externally-applied DC magnetic fields. In addition, two novel microstrip-based test structures were used to extract the complete set of microwave properties and their dependence on externally-applied magnetic field. The transmission of microwave signals through these structures is susceptible to variation in the dielectric/magnetic properties of the polymer nanocomposites, which facilitates the demonstration of the tunability and extraction of properties at different magnetic field strengths.

The required magnetic field is achievable by small commercial permanent magnets, which justifies the use of this new class of materials for implementation of practical microwave and RF devices and circuits. Magnetic polymer nanocomposites are very easy to process, which enables them to be employed in both PCB board and chip levels using conventional manufacturing processes. They exhibit unique and very attractive properties for many microwave applications that require tunability and flexible materials.

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