Thin Film
Room: 305 - Session TF+PS+SE-MoM

Advanced PVD Methods

Moderator: Subhadra Gupta, University of Alabama

9:00am **TF+PS+SE-MoM3 Ternary and Quaternary Thin Layers Deposited by Magnetron Sputtering**, ***Marie-Paule Besland***, *J. Tranchant, E. Janod, C. Benoit, L. Cario, P.Y. Jouan, M. Carette, A. Lafond*, Institut des Matériaux Jean Rouxel – Université de Nantes, France, *R. Meunier, S. Fabert*, Institut des Matériaux Jean Rouxel – Université de Nantes and Crosslux, France, *P.Y. Thoulon, M. Ricci*, Crosslux Company, France

Developing new functionalities mainly depend on the use of new functional material. Nevertheless, prior to envision any development of functional materials towards devices, two major challenges have to be tackled. The former one is to obtain thin layers of active and functional materials. The second challenge is to recover the functional properties on thin layers. For several decades, magnetron sputtering is a widely used deposition technique in microelectronics. Moreover, magnetron sputtering enables to deposit well-crystallized film of insulating or conducting materials, at low temperatures, over large areas, while controlling the film composition and microstructure, even for complex and multi-component materials. Thus, on the basis of well established know-how in deposition process and multi-layered functional structures [1], the deposition of GaV_4S_8 material in the form of thin layers has been investigated by both non-reactive RF magnetron sputtering and reactive process in Ar/H_2S mixture [2]. While the functionality (Resistive switching =RS) was first evidenced on single crystals, our studies demonstrated that metal-insulator-metal (MIM) structures based on GaV_4S_8 thin layers, deposited by magnetron sputtering, exhibit as well a similar RS [3]. More recently, we focus on the historical chalcogenide absorber for solar cells: CIGSe. We developed a dedicated and home-designed vacuum chamber for CIGSe thin films deposition using "one step sputtering". In that study, CIGSe thin films were deposited on SLG/Mo substrates by RF magnetron sputtering and then ex-situ annealed under controlled atmosphere. Deposition and annealing parameters can modify both chemical composition and structural properties. In particular, different preferential crystalline orientation may be induced and can modify functional properties in a large extend. Finally, the performances of CIGSe solar cell completely realized by magnetron sputtering technique will be compared to published efficiency values in the 8.9- 10.5 % range [5].

1- C. Duquenne et al. J. Appl. Phys. 104 (2008) 063301; M.P. Besland et al. Thin Solid Films 495 (2006) 86.

2- E. Souchier et al. Thin Solid Films 533 (2013) 54 ; J. Tranchant et al. J. Phys. D: Appl. Phys. 47 (2014) 065309.

3- J. Tranchant et al. Thin Solid Films 533 (2013) 61.

4- J. A. Frantz et al. Thin Solid Films 519 (2011) 776; A.J. Zhou et al. Thin Solid Films 520 (2012) 6068.

5- C. Chen et al. Solar Energy Materials & Solar Cells 103 (2012) 25; Thin Solid Films 535, (2013) 122.

9:20am **TF+PS+SE-MoM4 Molecular Dynamics Simulations of TiN/TiN(001) Growth**, ***Daniel Edström***, *D.G. Sangiovanni, V. Chirita, L. Hultman*, Linköping University, Sweden, *I.G. Petrov, J.E. Greene*, University of Illinois at Urbana Champaign

The Modified Embedded Atom Method (MEAM) interatomic potential within the classical Molecular Dynamics (MD) framework enables realistic, large-scale simulations of important model materials such as TiN. As a step toward s understanding atomistic processes controlling the growth of TiN on a fundamental level, we perform large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in excellent qualitative and good quantitative agreement with Ab Initio MD based on Density Functional Theory (DFT) [3], [4]. Half a monolayer of TiN is deposited on 100x100 atom TiN(001) substrates at a rate of 1 Ti atom per 50 ps, resulting in simulation times of 125 ns. The TiN substrate is maintained at a typical epitaxial growth temperature, 1200 K during deposition using Ti:N flux ratios of 1:1 and 1:4 with incident atom energies of 2 and 20 eV to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; the formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For equal flux ratios at 2 eV incidence energy, islands begin to form atop existing islands at coverages $\gtrsim$ 0.25 ML, leading to 2D multilayer growth. At 20 eV, the film growth mode shifts toward layer-by-layer growth. We discuss the implications of these results on thin film growth and process tailoring. Our classical MD predictions are supported and complemented by DFT-MD simulations.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiNx (x=1–3) admolecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, Oct. 2012.

[2] D. Edström, D. G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands," *Thin Solid Films*, vol. 558, pp. 37–46, May 2014.

[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N2 desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25–31, Jun. 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci (In Press)*. doi: 10.1016/j.susc.2014.04.007

9:40am **TF+PS+SE-MoM5 Surface Chemistry of Pd and Ag Interaction with 3C-SiC Thin Films Deposited on Si(111) by Pulsed Laser Depositon**, ***Rachel Seibert***, *D. Velazquez, J. Terry*, Illinois Institute of Technology, *K.A. Terrani, C. Baldwin, F. Montgomery, K. Leonard, J. Hunn, P. Schuck, R. Stoller*, Oak Ridge National Laboratory, *S. Saddow*, University of South Florida

The surface interactions of nuclear fission products with the barrier SiC layer of Tri-Structural Isotropic (TRISO) coated fuel particles limit fuel cell performance. In particular, Pd and Ag reduce the structural integrity of SiC. An understanding of the reaction mechanisms and kinetics of these interactions under normal operation as well as accident conditions is critical for the development of advanced nuclear reactors, but currently is not well understood. This surface chemistry is examined both in spent TRISO fuel on SiC/Si(111) thin films and compared to theoretical calculations done by Schuck and Stoller at Oak Ridge National Laboratory [1]. Synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy measurements were conducted on the irradiated TRISO fuel pellet to characterize atomic interactions at the Pd K-edge (24350 eV). The thin films were grown epitaxially via pulsed laser deposition (PLD), as evidenced by reflection high energy electron diffraction (RHEED) patterns. Pd and Ag were deposited on separate SiC/Si(111) films in thickness increments from 0.5-5 monolayers. The chemical structure of the thin films is analyzed using X-ray photoelectron spectroscopy (XPS).

[1] Schuck, P.C. and R.E. Stoller, *Ab initio study of the adsorption, migration, clustering, and reaction of palladium on the surface of silicon carbide.* Phys. Rev. B **83**, (2011)

10:00am **TF+PS+SE-MoM6 High Thermal Stability Nanocrystalline Gold, Part I**, ***Ronald Goeke***, *N. Argibay, J.E. Mogonye, K.M. Hattar, S.V. Prasad*, Sandia National Laboratories

Gold coatings that are ideally suited for low electrical contact resistance (ECR) applications are mechanically soft and exhibit unacceptable amounts of adhesion and friction. To mitigate these problems gold for ECR applications is typically alloyed with Ni, Co or Fe which increases the film hardness and wear resistance. A key limitation of hard gold coatings is the propensity for the non-noble alloying metal species to diffuse to the surface and form non-conductive oxide films that can severely impact the electrical contact behavior. These traditional hard gold films, which are fabricated via electro-deposition, have been limited to electrochemical compatible materials. Using co-deposition of Au-ZnO by electron beam evaporation we have eliminated the electrochemical material limitations and synthesized a new class of hard gold thin films. The ceramic phase is used to strengthen the composite via grain refinement. The resulting nanocrystalline gold thin film can replace typical hard gold films and exhibits enhanced thermal stability as the refractory ceramic phase is kinetically limited and has no oxidative potential for migration to the surface. The synthesis, characterization, and thermal stability against grain sintering will be discussed.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **TF+PS+SE-MoM8 High Thermal Stability Nanocrystalline Gold Thin Films, Part II**, ***Nicolas Argibay***, *J.E. Mogonye, R.S. Goeke, K.M. Hattar, M.T. Dugger, S.V. Prasad*, Sandia National Laboratories

In the second part we present the result of investigations of the bulk transport properties, thermal and mechanical stability, and mechanical properties of electron beam codeposited Au-ZnO as a function of composition and temperature (up to a homologous temperature of 0.5). A high throughput method for determining the average grain size in electrically conductive metal-ceramic thin films will be presented, founded on a correlation between grain boundary density and electrical resistivity (Mayadas-Shatzkes and Sondheimer-Fuchs models), and compared to microstructural characterization using backscatter and transmission electron diffraction, SEM, and XPS.

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11:00am **TF+PS+SE-MoM9 Growth and Phase Stability of Zirconium Diboride Thin Films**, ***David Stewart***, *D.J. Frankel, R.J. Lad*, University of Maine

Zirconium diboride (ZrB_2) has metallic-like electrical and thermal conductivities up to its melting point of 3246°C and is also thermal shock resistant, making it an excellent material for use in harsh, high temperature environments. Presently, much of the literature on boride materials concerns bulk, sintered materials, and less is known about ZrB_2 thin films. Here we demonstrate the growth of ZrB_2 thin films by e-beam co-evaporation of elemental Zr and B sources on sapphire, silicon, and silica substrates. Films were deposited over a range of Zr:B compositions and were characterized before and after annealing up to 1000°C in air or under vacuum (10-8 Torr). Scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) indicated that as-deposited films are homogeneous, with a smooth morphology and covalent bonding character. X-ray diffraction (XRD) revealed that films deposited at temperatures from ambient to 600°C are typically amorphous, and annealing in vacuum up to 1000°C can cause the formation of a ZrB_2 crystalline phase that coexists with an amorphous matrix, depending on the Zr:B ratio. Films annealed in air as low as 800°C become heavily oxidized and boron-depleted, leaving behind a monoclinic ZrO_2 polycrystalline film. XPS depth profiles suggest the formation of a boron oxide phase in air that evaporates from the surface at high temperatures, consistent with surface oxidation behavior reported for bulk ZrB_2 materials. Electrical conductivities of as-deposited films, measured with a 4-point probe, range from $0.3 – 8.3 \times 10^6$ S/m depending on the Zr:B ratio, and the films retain their conductive nature after vacuum annealing. The ZrB_2 crystalline phases exhibit a preferred (100) crystallographic texture, and valence band XPS measurements confirm the existence of hybridized B2p-Zr4d bonding states. Understanding the high temperature stability of ZrB_2 films is important for developing it as a potentially stable conducting film for electronic device applications in harsh environments.

11:20am **TF+PS+SE-MoM10 Thickness Dependence of High Frequency Magnetic Properties for Thin Films of Iron-Gallium-Boron**, ***Colin Rementer***, *Y. Kim, J.P. Chang*, University of California at Los Angeles

Iron gallium boron, i.e. $(Fe_{80}Ga_{20})_xB_{1-x}$ or FeGaB, is a material of considerable interest for high frequency, multiferroic applications. Lou *et al*. discovered that the addition of boron to the magnetostrictive material Galfenol ($Fe_{80}Ga_{20}$ or FeGa) led to a decrease in coercivity (~1 Oe), decrease in ferromagnetic resonance (FMR) linewidth (~20 Oe) at *X* band, and an increase in piezomagnetic coefficient (~7 ppm/Oe). The physical properties were optimized in $(Fe_{80}Ga_{20})_{88}B_{12}$ with ~100 nm thickness (Lou, J. et al. 2007). The material has been incorporated into several multiferroic systems with great success (Lou, J. et al. 2009). It is a material of great interest for integration into various multiferroic antenna systems. To have a better understanding of the material, a more thorough study on the fundamental properties of the material at different thicknesses is needed, as well as how that thickness can affect the tunability of resonant frequency and magnetoelectric coupling in multiferroic heterostructures when incorporated with ferroelectric single crystals.

FeGaB was grown via co-sputtering of $Fe_{80}Ga_{20}$ and boron targets via DC magnetron and RF magnetron sputtering, respectively. The FeGa target was held at 60 W and the boron power was adjusted to tune the boron concentration, from 9 - 18%. FeGaB films were grown with thicknesses ranging from 30 nm – 500 nm, and a growth rate of 7 nm/min was achieved. The coercivity and saturation magnetization of the FeGaB films decreased (~10 Oe), and increased (1200 emu/cc), respectively, with decreasing thickness (30 nm). Ferromagnetic resonance (FMR) linewidth was measured at *X* band (9.6 GHz), and it was found that it narrowed to 140 Oe with decreasing thickness at 30 nm. Both $Fe_{75}Ga_{25}$ and $Fe_{60}Ga_{22}B_{18}$ were shown to be magnetoelastic, having magnetostriction constants of around 30 ppm and 60 ppm, respectively. The magnetic properties of FeGaB are being optimized to the properties measure by Lou et al. to ensure the rigor of the thickness dependence study (Lou, J. et al. 2007). The effect of inducing stronger in-plane anisotropy in the FeGaB films was investigated via an *in situ* magnetic field applied during deposition, and post-deposited magnetic annealing is being explored as a function of thickness.

11:40am **TF+PS+SE-MoM11 Optimizing Magnetic Confinement for High Productivity PVD System Linear Scanning Magnetron**, *V. Kudriavtsev*, ***Robert Norris***, *T. Bluck, I. Latchford*, Intevac, Inc.

High productivity vacuum PVD system cost of ownership is very sensitive to sputtering target utilization. In this paper we discuss magnetic array design methodology that is required to achieve excellent plasma confinement that can lead to most uniform target erosion both magnetic and nonmagnetic targets. Design trade-offs are more challenging when using highly magnetic target materials, such as Nickel. These materials have lower PTF (pass through flux) and also affect magnetic field in all directions. Stronger magnets allow the fields to penetrate magnetic target material and judicious design process allows minimizing negative effects of field shunting.

First we develop static magnetic simulations model; magnetic properties are assigned to magnets, magnetic materials and also properties to nonmagnetic elements. Resulting computations are presented in a form of magnetic field component and Bz component on the surface of the target or in the vicinity of that surface. The magnetic track is determined by searching for locations where perpendicular component of magnetic field Bz=0 and we review variations in Bx and By along this track. Magnetic field characteristics are studied at various distances from magnets, sizing the magnetic array configuration, magnet dimensions, and their polarity for a selected objective. Usually this objective is to provide certain field strength at certain distance away from magnets. One can increase the strength of N or S polarity in the array, creating balanced or unbalanced magnetron configuration, that affect maximum field strength, erosion profile and erosion in the middle of the target where the absolute value of magnetic field reaches a maximum. Magnetic field characteristics are extracted from the erosion track profile and theoretical erosion profile is calculated resulting from the current array design. These profiles allow estimation of the “static” target utilization and if necessary to create optimization cycle where magnetic characteristics of the design (parameters) are computationally changed to reach desired erosion profile. Once the final computer design is selected, engineers build the first prototype of magnetic array and evaluate its magnetic properties using a 2d magnetic scanner that provide B, Bx, By, Bz components of magnetic field in plane on a distance from magpack. The next step of the analysis utilizes experimentally extracted magnetic field (or previously computed theoretical magnetic field) to estimate resulting 2D erosion profile that is due to the magnet non-uniform and non-linear motion. Finally, using the ray tracing method we perform film uniformity analysis for a substrate of given size which is located on a defined distance away from the sputtering target. That analysis is transient and factors in substrate nonlinear motion. Resulting film uniformity is estimated as a superposition of multiple substrate positions as it moves under the target.

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