Spectroscopic Ellipsometry Focus Topic
Room: 112 - Session EL+AS+BI+EM-ThA

Optical Characterization of Nanostructures and Metamaterials
Moderator: Bernard Drevillon, LPICM-CNRS, Ecole Polytechnique, France, Mathias Schubert, University of Nebraska - Lincoln

2:20pm **EL+AS+BI+EM-ThA1 Electrostatic Coating with Ligandless Copper Nanoparticles**, ***Lance Hubbard***, *A.J. Muscat*, University of Arizona

Electroless deposition (ELD) produces conformal coatings at low temperatures. ELD occurs by chemical reduction of metal ions without an externally applied potential or catalyst layer. In this paper, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) native oxide was hydroxylated and terminated with a self-assembled amine layer (4 mM (3-aminopropyl)-trimethoxysilane in methanol). Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol (reducing agent), and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The Cu particle ion shell is attracted to the positively charged amine groups at high pH depositing a thin metal film that is both continuous and cohesive. Annealing the coupons at 200^{o}C in nitrogen promoted electrically conductive film formation. Electron microscopy images of the coated substrates showed a 80-95 nm thick film of 3 nm diameter particles. Four-point probe measurements of the films yielded electrical conductivities in the range 10^6-10^7 S/m (10-80% of bulk conductivty). The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.56 nm. Scanning electron microsopy (SEM) images at various angles in relation to the films were taken to examine film morphology and thickness. Spectroscopic ellipsometry (SE) data were modelled with bulk, nanophase d-band transition, and SPR absorbances. The SE agreed well with UV-VIS results for the SPR and shows an increasing contribution from d-band transitions with increasing ionic liquid concentration. SEM and Fourier transform infrared (FTIR) spectroscopy were used to determine film thicknesses and chemistry.

2:40pm **EL+AS+BI+EM-ThA2 Using Plasmonic Effects to Design Ellipsometric Targets with Sub-Angstrom Resolution**, ***Samuel O'Mullane***, SUNY Polytechnic Institute, *J. Race, N. Keller,* Nanometrics, *A.C. Diebold*, SUNY Polytechnic Institute

For traditional ellipsometric targets, slightly changing the thickness of a layer or the index of refraction of a material results in a similarly small change in the observed spectra. If structures are designed to allow for plasmonic coupling, a slight change in those same parameters results in wildly different spectra. Specifically, localized plasmonic resonances in metallic grating structures allow for extraordinary sensitivity to parameters such as CD, sidewall angle and pitch.

Existing metallic grating structures are arrays of long, thin lines of copper that can be described using one dimension. The typical resolution for ellipsometric CD measurements on these structures ranges from nanometers to Ångströms. Because there is no confining second dimension, localized plasmons cannot be produced.

In order to obtain sub-Ångström resolution, additional structural modifications are required. This is achieved by adding a second metallic grating perpendicular to the original grating forming a cross-grating structure. Note that the added pitch and linewidth are an order of magnitude larger than the original parameters. This results in fully localized plasmonic resonances so that parameter variation on the order of tens of picometers could be detected through ellipsometric measurements. Making use of conical diffraction further increases the sensitivity to structural changes due to increased anisotropy.

These conclusions are the result of rigorous coupled wave-analysis (RCWA) simulations which were confirmed via finite element method (FEM) simulations. With both RCWA and FEM agreement, experimental confirmation is expected.

3:00pm **EL+AS+BI+EM-ThA3 Enhanced Temperature Stability of Slanted Columnar Thin Films by ALD Overcoating**, ***Alyssa Mock***, *D. Sekora, T. Hofmann, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

The demand for thermally stable nanostructures continues to increase as nanotechnology becomes ever more prevalent in both commercial and research applications. The high surface area of nanostructured thin films is susceptible to degradation under extreme temperatures. Scanning electron microscopy (SEM) and Mueller Matrix Generalized Ellipsometry (MMGE) were used to observe optical and structural properties of a glancing angle deposited cobalt slanted columnar thin film (SCTF) over increased annealing temperature. We show that the use of atomic layer deposition (ALD) to conformally passivate the SCTF surface provides both physical scaffolding and thermal protection during the annealing process up to 475°C as no changes in the SEM or MMGE results were present.

3:20pm **EL+AS+BI+EM-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Heat Treated Sculptured Thin Films: A Study of the Effects of Al_2O_3 Passivation Coatings on Magneto-Optical Properties**, ***Chad Briley***, *A. Mock,* University of Nebraska-Lincoln, *D. Schmidt,* National University of Singapore, *T. Hofmann, E. Schubert, M. Schubert*, University of Nebraska-Lincoln

We present the vector magneto-optical generalized ellipsometric (VMOGE) response[1] and model dielectric function (MDF) anisotropic hysteresis calculations[2] of ferromagnetic slanted columnar thin films under the effects of heat treatment up to 475° C. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on Cobalt slanted columnar thin film samples grown by glancing angle deposition with and without Al_2O_3 conformal passivation overcoating done by atomic layer deposition. Analysis of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determine the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor displays anisotropic magnetic response of the thin film with the hard axis along the long axis of the columns. Data analysis reveals the preservation of anisotropic magneto-optical properties of the thin film with the passivated coating as compared to the non-passivated coating due to oxidation effects from heat treatment.

[1)] D. Schmidt, C. Briley, E. Schubert, and M. Schubert, Appl. Phys. Lett. **102**, 123109 (2013).

[2)] C. Briley, D. Schmidt, T. Hofmann, E. Schubert, and M. Schubert, Appl. Phys. Lett. **106**, 133104 (2015).

4:00pm **EL+AS+BI+EM-ThA6 Spectroscopic Ellipsometry for Critical Dimensions Analysis**, ***Vimal Kamineni***, GLOBALFOUNDRIES, *D. Dixit, S. O'Mullane,* SUNY Polytechnic Institute, *G. Iddawela, A. Vaid,* GLOBALFOUNDRIES, *A.C. Diebold*, SUNY Polytechnic Institute **INVITED**

In this talk an overview of the current applications of spectroscopic ellipsometry (SE) towards measuring the shape of nanostructures will be presented. The transition of the semiconductor industry from planar to 3D transistors has expanded the applications of ellipsometry. Ellipsometry measurements on the periodic nanoscale structures enable a diffraction based measurement technique referred to as scatterometry. The critical dimensions can be extracted by means of a regression on the diffracted light using rigorous coupled wave analysis (RCWA). RCWA is a Fourier-space method used to generate the optical response by slicing the periodic structure of interest and matching the boundary conditions to compute EM modes. This method is inherently dependent on *a priori* knowledge of the dielectric function of the materials that construct the nanostructures as well as the shape of the nanostructure obtained from reference metrology. Furthermore, time-to-solution is one of the main drawbacks of developing scatterometry applications due to the dependency on developing a robust model and for validating the model with reference metrology measurement. To address these challenges new methods such as signal response metrology (SRM) encompassing machine-based statistical learning and virtual reference metrology have been proposed. [1,2] These methods will be reviewed along with their benefits and limitations when applied to advanced 3D transistor structures. In addition, application of Mueller matrix ellipsometry measurements on strained grating structures (SiGe/Si) and block copolymer structures to determine the impact of strain and defectivity (bridging defects, wiggles, LER, etc.) on anisotropy coefficients will be presented, respectively. [3,4] Additionally, hybrid approaches will be proposed in conjunction with complementary/supplementary metrology methods (CD-SEM, HRXRD and CD-SAXS). [5-7]

[1] S. Pandev et al., SPIE Proc. 9424 (2015).

[2] A. Vaid et al., SPIE Proc. 9424 (2015).

[3] G. R. Muthinti et al., SPIE Proc. 8681 (2013).

[4] D. J. Dixit et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 14, 021102 (2015).

[5] A. Vaid et al., SPIE Proc. 8324 (2012).

[6] A. C. Diebold et al., Proceedings of SPIE 8681, 86810I (2013).

[7] Charles Settens et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 13, 041408 (2014)

4:40pm **EL+AS+BI+EM-ThA8 Structural and Ellipsometric Analysis of the Topological Insulator Bi_2Se_3**, ***Avery Green***, SUNY Polytechnic Institute

Topological Insulator (TI) materials have been the subjects of increasing scientific interest in the last decade. Their spin-momentum locked Dirac cone surfaces and insulating bulks have resulted in new directions in physics research and new spintronic devices. Though these materials have been thoroughly described in theory, the experimental realization and measurement of these surface states has been problematic, due to various crystalline defects. Theory predicts that TI surface states are protected against local defects, but it is essential to study the effects of global perturbations caused by surface oxidation, stoichiometric aberrations, and significant structural defect densities. The aim of this study is to measure the time-dependent dielectric function of the Bi_2Se_3 surface and bulk in air, using a dual rotating compensator spectroscopic ellipsometer. These data are backed up with various metrological measurements (AFM, cross-sectional TEM, EDS) to confirm surface topology and oxide thickness. This analysis of optical properties and oxide formation will, in the future, be used to optimize the Bi_2Se_3 flake thickness identification process, and provide a control for further necessary structural analysis, as stated above.

5:00pm **EL+AS+BI+EM-ThA9 Visible Luminescence in the VLS Grown Self Ga Doped ZnS Nanostructures**, ***Arshad Bhatti***, *H. Hussain, M.A. Johar, S. Rehman, M.A. Shehzad, M.A. Hafeez*, COMSATS Institute of Information Technology, Pakistan

ZnS is a wide band gap semiconductor and thus offers fascinating opportunities for tailoring and tuning its bandgap states for photonic devices in visible region of the spectra. Ga introduced a strong red luminescence in ZnS. VLS mechanism was employed to synthesize ZnS nanowires using Ga as a catalyst and dopant simultaneously. The thickness of Ga ultrathin film was varied from 0.5 nm to 5 nm to observe the effect of Ga droplet size on the formation, lifetime and activation energies of defect states in the band gap. It was expected that Ga^{3+} would replace Zn^{2+} sites and dope ZnS, in addition, an impurity phase of Ga_2S_3 was also observed, whose content showed strong dependence of Ga thickness. It also shrunk the crystallinity of ZnS due to varied size of Ga^{3+}(76 pm) ions replacing Zn^{2+} (88 pm), which was observed in the shifts of major XRD reflections of ZnS. Incorporation of Ga introduced strong impurity states in the band gap of ZnS. It also affected the intrinsic defect states of ZnS, namely Zn and S vacancies (Please refer to Figure 1, which also shows the de-convoluted band gap broad band). In the PL spectra, blue (440 nm), yellow (560 nm), orange (600 nm) and red (680 nm) bands were attributed to S vacancies, Ga related defects, donor-acceptor recombination and Ga_2S_3, respectively. Photoluminescence excitation spectroscopy revealed strong absorbance at corresponding energies. A strong correlation of these states was observed in the temperature dependent PL measurements due to presence in their presence in the vicinity as the activation energies of these states matched the energy differences of corresponding states. The conductivity measurements also complimented the optical results. Time resolved PL demonstrated the lifetime of these states was between 0.5 ns to 1.5 ns and had somewhat significant effect of dopant concentration. Finally, Ga doped ZnS showed extremely efficient IR sensitivity.

Figure 1: The room temperature PL spectra of Ga doped ZnS nanowires synthesized with varied thickness of Ga: (a) 0.5 nm, (b) 1.0 nm, (c) 3.0 nm, and (d) 5.0 nm. The broad band between 450 nm to 750 nm has been de-convoluted to show contribution of various defect states (as mentioned in the Figure). These states were identified from the PLE spectrum.

5:40pm **EL+AS+BI+EM-ThA11 Can Front-Surface Metal Mirrors Be Protected from Oxidation by Vacuum Applied Polymer Films?**, ***David Allred***, *R.S. Turley*, Brigham Young University, *R.T. Perkins*, Utah Valley University

We have used variable-angle, spectroscopic ellipsometry to monitor secular changes in multilayers consisting of chemically active thin films, such as aluminum, deposited on dielectric-coated silicon wafers and protected by various vacuum-applied barrier layers. Ultrathin barrier layers included polymers such as parylene and rarely, sputtered inorganic films, such as silicon. Applications include the measurements of the oxidation of evaporated aluminum for use as a mirror in the VUV (vacuum ultraviolet) and the determination of the optical constants of materials such as Y_2O_3 potentially useful in VUV and XUV (extreme ultraviolet) optics.

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