Spectroscopic Ellipsometry Focus Topic
Room: Cochiti - Session EL+AS+EM+MS+TF-FrM

Spectroscopic Ellipsometry - Inorganic Thin Films
Moderator: L.A. Giannuzzi, L.A. Giannuzzi & Associates LLC

8:20am **EL+AS+EM+MS+TF-FrM1 Spectroscopic Ellipsometry Study on Transparent Conductive Ga-doped ZnO Thin Films Deposited by Ion-Plating with DC Arc Discharge**, *T. Yamada, **H. Makino**, N. Yamamoto, T. Yamamoto*, Kochi University of Technology, Japan

Transparent conductive Ga-doped ZnO (GZO) thin films was one of promising candidates as transparent electrodes in flat panel displays and thin film solar cells. In this study, we investigated contributions of intra-grain scattering and grain boundary scattering on Hall mobility of polycrystalline GZO thin films based on the analysis of spectroscopic ellipsometry measurements. The GZO films were deposited by ion-plating method with DC arc discharge. Samples with a wide range of thicknesses from 70 to 500 nm were deposited at 200 degree C on glass substrates by controlling the deposition time. Sintered ZnO ceramic tablets doped with 1 wt% and 4 wt% Ga_2O_3 were used as evaporation sources. A systematic study has been done on the structural, electrical and optical properties of GZO films. In the case of GZO films using 4wt% Ga_2O_3 doped tablet, the minimum resistivity of 1.8×10^{-4} Ωcm was obtained at the film thickness of around 350 nm. The carrier concentration and Hall mobility was 1.2×10^{21} cm^{-3} and 29 cm^2/Vs, respectively. The GZO films showed c-axis preferential orientation nearly normal to the substrate surface with columnar grain structures. In XRD measurements, full width half maximum of (0002) omega rocking curve decreased with increasing the film thickness. It means that the fluctuation in the c-axis orientations among the grains improved with increasing the film thickness. Average grain size of columnar structure was estimated by Williamson-Hall plot on spectral width of in-plane XRD patterns. The average grain size increased with increasing film thickness. Optical mobility of the GZO films was estimated from analysis using the conventional Drude model on data obtained by spectroscopic ellipsometry. Differences between the optical mobility obtained by the spectroscopic ellipsometry and the Hall mobility obtained by Hall effect measurements suggest contribution from grain boundary scattering on the Hall mobility. It demonstrates that grain boundary scattering contributes to the Hall mobility in rather thinner film thickness. However, the very small contribution of grain boundary scattering to the Hall mobility was observed in the thick films. On the other hand, resistivity of 4.5×10^{-4} Ωcm with the carrier concentration of 3.6×10^{20} cm^{-3} and Hall mobility of 39 cm^2/Vs was obtained for a 500 nm thick GZO film using the ZnO ceramic target doped with 1 wt% Ga_2O_3. The spectroscopic ellipsometry analysis on the GZO film suggests that the Hall mobility was dominated by intra-grain scattering.

8:40am **EL+AS+EM+MS+TF-FrM2 Spectroscopic Ellipsometry of Pulsed Laser Deposited ZnO on Atomic Layer Deposited Al_2O_3 and HfO_2**, ***D.L. Agresta**, K.D. Leedy*, U.S. Air Force Research Laboratory

Zinc oxide thin films and coatings are an integral part of a number of devices because of their wide range of properties. Depending on the conductivity and transparency, these materials are of interest for electronic (diodes, FETs), optoelectronic (detectors, modulators, flat-panel displays, solar cells, etc.) and piezoelectric (BAW,SAW) devices. In this study, we examine FET ZnO active device layers in conjunction with atomic layer deposited (ALD) Al_2O_3 and HfO_2 for isolation and gate dielectrics. Stacks of pulsed laser deposited (PLD) ZnO on thermal and plasma ALD Al_2O_3 and HfO_2 are prepared on a variety of large area substrates.

The surface morphologies of PLD grown ZnO-based films and ALD dielectrics are critical to optimize the interface quality in multilayer structures. Therefore, the control and optimization of surface properties over large areas is essential for the successful application of PLD ZnO thin films in device configurations. We have previously reported high quality ZnO films being obtained over large areas using off-axis PLD [1, 2]. Film thickness and compositional uniformity control is a critical issue associated with the scale-up of PLD systems. Thus, spectroscopic ellipsometry (SE) has a significant role in the characterization of these films.

A commercial Phase-Modulated Ellipsometer (PME) is employed to study the interplay between structural, electrical and optical properties of single-layers and PLD ZnO/ALD dielectric stacks. Known for its precision and non-destructiveness, SE is an indirect measurement technique in the sense that the film properties of interest are obtained by a nonlinear regression analysis of measured data to an optical model. We examine the effect on the goodness of fit parameter from the use of various optical models. Furthermore, since we are employing a PME, the time to scan a wide spectral region is limited by the slew rate of the monochromater. This can be a significant burden when making uniformity determination over large-area substrates. Thus, we examine the effect on the goodness of fit parameter from minimizing data acquisition time. The optical properties of the individual thin films extracted by SE are compared to optical studies using normal incidence transmission. Film surface roughness is obtained from SE by employing the Bruggeman effective-medium approximation and subsequently compared to structural characterizations using atomic force microscopy and x-ray diffraction.

Reference:

K. D. Leedy, C. V. Varanasi, D. H. Tomich and B. Bayraktaroglu, 5th International Workshop on ZnO and Related Material (2008).

2. D. Agresta, K. Leedy, R. Scott, T. Dang and B. Bayraktaroglu,, AVS-56 (2009).

9:00am **EL+AS+EM+MS+TF-FrM3 Processing and Stability Studies of Vanadium Oxide Thin Films for Microbolometer Applications**, ***M.A. Motyka**, B.D. Gauntt, E.C. Dickey, M.W. Horn, N.J. Podraza*, Penn State University

Vanadium oxide (VO_x) thin films are commonly used as an imaging material in uncooled infrared sensing devices. Material properties that make VO_x useful for this application are a high temperature coefficient of resistance (TCR), controllable resistivity (ρ), and low electrical noise. A difficulty in growing VO_x thin films arises from the many valence states of vanadium, which may result in formation of a film consisting of an undesirable phase or with the presence of multiple phases. Each phase has varying electrical properties and thus, the reliability and consistency in industrial fabrication is lowered. Furthermore, atmospheric exposure of the VO_x films has been shown to alter the electrical and optical properties. In order to prevent changes in the desired material, VO_x films are commonly capped with a thin layer of SiO_2 before atmospheric exposure. In this study, vanadium oxide thin films were studied using in situ real time spectroscopic ellipsometry (RTSE) over a spectral range of 0.75 to 5.15 eV during deposition via pulsed DC-magnetron sputtering in an argon and oxygen atmosphere, with the set of variables being the total pressure, the oxygen-to-argon ratio, target power and the target material (metallic V, VO_2, V_2O_5). These variables control the material growth and resulting optical and electrical properties. The growth evolution, complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), and structure obtained from RTSE have been shown to correlate with the electrical properties of the film. Ex situ Fourier transform infrared spectroscopic ellipsometry (FTIR-SE) measurements were also made to help characterize the materials in the spectral range of 0.05 to 0.75 eV, so that the optical properties in the range of microbolometer operation are obtained. Electrical measurements include temperature dependent I-V curve measurements to determine the VO_x film resistivity and TCR as a function of processing conditions. Changes in the optical and electrical properties as a function of processing conditions including film thickness are explored for materials exhibiting amorphous or nanocrystalline (V, V_2O, and VO phase) structures. RTSE is also used to monitor the changes in optical properties of the VO_x layer and interfacial formation arising from the deposition of the SiO_2 capping layer. The environmental stability of VO_x with and without capping layers is also monitored via RTSE as the samples are initially exposed to the atmosphere after deposition. In this manner both intentional variations in film microstructure and electrical properties as a function of processing conditions and unintentional variations arising from material instability are studied.

9:20am **EL+AS+EM+MS+TF-FrM4 Instrumentation of Far-infrared Mueller Matrix Ellipsometer and Its Application for Multiferroic Materials**, ***T.D. Kang**, P.D. Rogers, E. Standard, G.M. Nita, T. Zhou,* New Jersey Institute of Technology, *G.L. Carr,* Brookhaven National Laboratory, *S. Zollner,* IBM Systems and Technology Group, *M. Kotelyanskii,* Rudolph Technologies, Inc., *A. Sirenko*, New Jersey Institute of Technology

We develop a far-IR spectroscopic ellipsometer at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL). This Ellipsometer is designed to measure a full-Mueller matrix of the sample by using compensators and wire-grid linear polarizers [1]. With the exceptional brightness of synchrotron radiation and the Fourier-transform infrared (FT-IR) spectrometer, we measure ellipsometric data with a high accuracy at multi-wavelengths between 10 and 4,000 cm^{-1}. Study in terms of temperature variation of the sample is available using the cryostat for temperature between 4.2 K and 450 K. The wide range of θ-2θ rotation, c angle adjustment, and X-Y-Z translation of sample stage enables high accuracies in the alignment, calibration, and ellipsometric measurement.

With the Labview program interface, the automated experiments with the pre-programmed measurement schedules are performed by controlling the motors, temperature, and FT-IR spectrometer. The ellipsometric data analysis is based on the Berreman 's 4×4 propagation matrix formalism [2] to extract dielectric permittivity and magnetic permeability tensors for bulk and thin film samples from the Mueller matrix measured at variable incidence angles and sample orientations across the broad far-IR spectral range. Applications of this far-IR ellipsometry for multiferroic materials with $\mu \neq 1$ will be discussed. This development effort is supported by NSF-MRI-0821224.

[1] P. S. Hauge, J. Opt. Soc. Am. 68, 1519 (1978).

[2] D.W. Berreman, J. Opt. Soc. Am. **62**, 502 (1972).

9:40am **EL+AS+EM+MS+TF-FrM5 Roughness beyond Bruggeman's Effective Medium Approximation**, ***H. Wormeester***, University of Twente, Netherlands **INVITED**

Surface roughness is regularly characterized with ellipsometry, which is especially sensitive for the short length scale roughness. Because of this, the roughness can be treated as a heterogeneous material modelled with an Effective Medium Approximation (EMA). The EMA layer thickness determined is often successfully related to the root mean square roughness from microscopy. A breakdown of this correspondence was recently shown [1]. This was attributed to the non-negligible influence of the characteristic length scale of the roughness. This typical characteristic length scale can approach the wavelength of the light used for many cases of surface roughness. In thus violates an important prerequisite of EMA, i.e. a variation limited to a length scale much smaller than the wavelength of light. This not only results in off-specular scattering, but also to a change in the polarization of the specular reflected light beam as probed with ellipsometry.

The applicability of an EMA to describe small surface roughness can be evaluated with the Rayleigh-Rice (RR) perturbation. In this perturbation method, the surface roughness is incorporated via its power spectral density function. Ohlidahl and co-workers [2] extensively compared Gaussian roughness distributions with EMA results. They reported that Bruggeman's equation describes the roughness well in many situations. However, the correspondence between EMA and RR breaks down for surface heterogeneity if noble metals are involved. For example for deposited colloids, the resonance energy of the induced surface plasmon is not correct [3]. Also the optical spectra calculated with EMA for a rough silver surface can only be reproduced by RR if a very specific power spectral density is used, showing a quite large characteristic length scale.

Roughness with various length scales created by oblique incidence ion sputtering on Ag(001) were experimentally studied with normal incidence ellipsometry, also known as Reflection Anisotropy Spectroscopy [4]. The observed plasmon resonances are the result of anisotropy in the local length scale. This system allows to probe quantitatively the adequacy of the RR. One of the limits discussed is the inability to discriminate between roughness and roughness length scale for small scale roughness. The ability to monitor in-situ the evolution of the anisotropy of the roughness distribution will be addressed.

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10:20am **EL+AS+EM+MS+TF-FrM7 Spectroscopic Ellipsometry on Graphene**, ***J.W. Weber***, Eindhoven University of Technology, Netherlands, *V.E. Calado*, Delft University of Technology, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

We show how we used spectroscopic ellipsometry to determine both the optical constants and thickness of graphene1. We scanned a mechanically exfoliated graphene flake (150 x 380 μm) on an oxidized silicon wafer (98 nm SiO2) with a spectroscopic ellipsometer with a focused spot (100 x 55 μm) at an angle of 55°, in the range 210-1000 nm. The spectroscopic ellipsometric data were analyzed with an optical model in which the optical constants of graphene were parameterized by B-splines.2,3 This parameterization was key in the uncorrelated, accurate and simultaneous determination of the optical constants and thickness of graphene. The thickness is in perfect agreement with the thickness as expected from the interlayer spacing in graphite: 3.4 Å. This work opens up the possibility for in situ monitoring of graphene growth.

References

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[2] B. Johs and J. S. Hale, *Phys. Status Solidi A* **205**, 715 (2008).

[3] J. W. Weber, T. A. R. Hansen, M. C. M. van de Sanden, and R. Engeln, *J. Appl. Phys.* **106**, 123503 (2009).

10:40am **EL+AS+EM+MS+TF-FrM8 Free-charge Carrier Properties of Epitaxial Graphene by Terahertz and Infrared Ellipsometry**, ***T. Hofmann***, *A. Boosalis, P. Kühne,* University of Nebraska-Lincoln, *J.L. Tedesco, R.L. Myers-Ward, P.M. Campbell, C.R. Eddy, Jr., D.K. Gaskill,* U.S. Naval Research Laboratory, *V. Shields, S. Shivaraman, M.G. Spencer, W.J. Schaff,* Cornell University, *M. Schubert*, University of Nebraska-Lincoln

Graphene systems exhibit extremely high charge carrier mobilities highly suitable for the design of high speed terahertz (THz), Angstrom scale transistors [1]. The use of graphene for future electronic devices requires the growth of epitaxial graphene layers on suitable substrates.

We have grown highest-quality epitaxial graphene on Si- and C-faces of silicon carbide substrates under various conditions. We report on Terahertz (THz), Far-infrared (FIR) and Infrared (IR) ellipsometry and THz-IR Optical Hall-effect (generalized ellipsometry in magnetic fields) investigations of the free-charge carrier properties in epitaxial graphene samples. Furthermore, new developments on the tunable-wavelength frequency-domain THz ellipsometry instrumentation with and without external magnetic will be described [2,3].

Our ellipsometric data allows the identification of multiple, parallel sheet carrier densities within the single-to-few monolayer thick graphene layers, and which crucially depend on substrate orientation and growth condition. Analysis of the multiple two-dimensional carrier sheet densities reveals their extreme yet strongly varying mobility, effective mass, and density parameters as well as the vertical carrier sheet profile. Our findings reveal striking influences of the substrate. We discuss the physical mechanisms of the substrate that influence the free-charge carrier properties in epitaxial graphene such as surface polarity, dopant incorporation, surface roughness, and defects. We present a free-charge carrier model for epitaxial graphene, its implications due to the substrate, and discuss in light of previous implementations [4].

References:

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[4] Z. Q. Li, *et al.*, Nature Physics **4**, 532 (2008).

11:00am **EL+AS+EM+MS+TF-FrM9 Mueller-Matrix Studies of Scarab Beetles using Spectroscopic Ellipsometry and Imaging Polarimetry**, ***H. Arwin***, Linköping University, Sweden, *S. Manhas,* LPICM, CNRS, Ecole Polytechnique, France, *J. Landin, K. Järrendahl,* Linköping University, Sweden, *A. De Martino*, LPICM, CNRS, Ecole Polytechnique, France

Many scarab beetles exhibit astonishing structural colors and polarization phenomena including circular polarization in the reflected light. Electron microscopy studies reveal that the cuticles of these beetles contain complex layered and/or chiral structures. From an applications point of view it is of large interest to explore these nanostructures as inspiration for biomimetic design based on structural colors and/or polarization.

In this work, spectroscopic ellipsometry as well as imaging polarimetry are used to determine normalized Mueller matrices of cuticles of several scarab beetle species. Mueller-matrix data in the visible spectral range are measured with a dual-rotating compensator ellipsometer. In addition real-space as well as Fourier-space Mueller-matrix images are recorded at 532 nm and 632 nm with an imaging polarimeter utilizing a microscope objective with a high numeric aperture.

The M41 Mueller-matrix element measured on the partly blue and partly green *Coptomia laevis* is very small and represents a beetle with a nanostructure without chirality. *Anoplognathus frenchi* is goldish and has a broad-band reflection with large values on M41. Very pronounced left-handed polarization effects are observed. *Cetonia aurata* has a narrow-band reflection and the color varies from green to red among species. In the color range of reflection, strong left-handed polarization is observed. Some beetles are also found to reflect right-handed polarization at certain wavelengths and angles of incidences.

The real-space Mueller-matrix images carry information about lateral variation of Mueller-matrix elements. In many cases beetle surfaces are laterally inhomogeneous. On the other hand, Fourier space images provide the azimuthal and angle of incidence variations of the Mueller-matrix elements, averaged over the spatial inhomogeneities. The Mueller-matrix

images are found to be consistent with the spectroscopic Mueller-matrix results and provide complementary information. The spectral Mueller-matrix data are also used for modelling the nanostructure of beetle cuticles involving dielectric surface layers and heliocoidal structures. Parameterization in terms of layer thicknesses, refractive indices and pitch of the helix in cuticle structures are presented.

11:20am **EL+AS+EM+MS+TF-FrM10 Agent-Free Bio-Chemical Sensing with Sculptured Thin Films**, ***D. Schmidt***, *K.B. Rodenhausen, S. Schöche, T. Hofmann, E.B. Schubert, M. Schubert*, University of Nebraska-Lincoln

A new concept of agent-free highly sensitive bio-chemical sensing is presented based on the change of birefringence of sculptured thin films (STFs). A mere intermixture of liquid or gaseous molecules with solid state STFs dramatically changes the overall optical properties of the porous film, which can be easily detected by means of ellipsometry or even the bare eye, i.e. light intensity changes upon interaction.

Previously, we have shown that STF exhibit highly anisotropic optical properties, which differ significantly from their bulk properties. Strong form birefringence and large dichroism can be tailored by appropriate deposition geometries to produce desired optical responses. In order to vary structure spacing (void fraction), and enable growth on defined sites self-assembled large-scale substrate patterning by diblock copolymer nanolithography can be exploited. We have demonstrated that generalized spectroscopic ellipsometry is ideally suited for determining geometrical structure and the anisotropic optical properties of STFs [1-3]. Recently, we have demonstrated that the combination of spectroscopic ellipsometry (SE) with quartz crystal microbalance (QCM) methods provides access to organic thin film thickness and porosity information and can further reveal structural properties of thin organic films [4].

Here we report on the application of STFs for bio-chemical sensing by simultaneous in-situ generalized ellipsometry (GE) and QCM measurements. STFs from different materials were deposited by glancing angle electron beam evaporation on gold-coated quartz crystals. Changes in the resonance frequency of the quartz crystals before and after STF deposition were used to determine the void fraction of the STF and agree well with scanning electron micrograph estimates.

In our in-situ experiments, we observe that the optical response of STFs is very sensitive to the ambient medium. We find that the filling of the STFs void fraction with solvents of different refractive index causes changes in birefringence as well as dichroism of the STFs.

Furthermore, the deposition of cetyltrimethylammonium bromide (CTAB), a well-known detergent molecule, is used here in order to demonstrate the detection of organic molecules. We find that the intriguing optical response of the STFs is changing drastically with the deposition of minute amounts of CTAB.

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