Thursday Afternoon, October 21, 2010

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

Spectroscopic Ellipsometry
Moderator: A.M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm **EL+AS+EM+MS+TF-ThA1 Developments in Spectroscopic Ellipsometry for Characterization of Organic and Inorganic Surfaces, Interfaces and Complex Layered Materials**, ***M. Schubert***, University of Nebraska - Lincoln **INVITED**

In this paper we will review new developments in Spectroscopic Ellipsometry for characterization of organic and inorganic surfaces, interfaces and complex layered materials. Ellipsometry has matured over the past two decades with instrumentation and methodology capable of addressing today's and tomorrow's challenges in materials characterization and metrology. Ellipsometry measures the general state of polarization of light reflected or transmitted from samples. Owing to its nondestructive and generally applicable concept of investigating light emerging from specimens under investigations, and owing to its extreme accuracy and precision, ellipsometry has paved the way for almost all our modern technologies, continues to enable next-generation devices in electronics and optoelectronics, and emerges into fields of chemical, biochemical and biological platform technologies. Originating from the identification that the information carried upon the polarization within a light beam emerging from surfaces is extremely sensitive to mono and submonolayer characteristics, ellipsometry started decades ago pioneering development of microprocessors and electronic devices, which still today are based on planar thin film technology. Without ellipsometry, today's computation and information technology would be still in its infancy. In this paper, emerging developments and applications for metrology of optical and electrical properties of semiconductors and nanostructures by Terahertz Magnetooptic generalized ellipsometry, also referred to as the Optical Hall effect, will be highlighted. Examples will include state-of-the-art nitride semiconductor device structures and epitaxial graphene, candidates for tomorrow's next-generation devices. Likewise, new approaches for characterizing precise structural, magnetic and optical properties of three-dimensional nanostructure hybrid materials will be discussed. Examples will describe how ellipsometry characterization enables understanding and tailoring of electromagnetic properties of materials created by human intelligence, rather than by nature. New horizons are being explored currently by combining ellipsometry with independent surface sensitive techniques, such as acoustic Quartz-Crystal microbalance techniques. Combinations allow for identification of new information not accessible otherwise. Examples include observation of in-situ formation of self-assembled monolayers, protein adsorption onto sensitized surfaces, and formation of micelle-assisted bilayer configurations. Prospects, challenges and future developments will be reviewed from today's perspective.

2:40pm **EL+AS+EM+MS+TF-ThA3 Characterizing the Adsorption – Desorption Behavior of Organic Molecules Within Thin Mesoporous Carbon Composite Films using Spectroscopic Ellipsometry**, ***B.D. Vogt***, *L.Y. Song, M.Z. Dai*, Arizona State University

Porous carbon materials are commonly utilized as adsorbants (i.e. activated carbon) and as catalyst supports. Direct templated synthetic routes to form ordered mesoporous carbons have recently been developed. By utilizing these concepts, mesoporous carbon composite films containing metal oxides can be synthesized. As a wide range of metal oxides can be utilized, these materials could be utilized in chemical sensing applications or as catalysts in fuel cell membranes. For both of these applications, the porous material will be exposed to organic vapors (such as ethanol in fuel cells). The condensation and evaporation of organic vapors from these materials is therefore an important consideration for their ultimate utilization in these applications. In-situ spectroscopic ellipsometry measurements of the mesoporous films exposed to controlled vapor pressures of organic vapors such as toluene, hexane and ethanol are utilized to understand the adsorption-desorption behavior of these films. Activated desorption of all three compounds is observed for pure carbon films, but addition of a small fraction of metal oxide enables the organics to be desorbed for the porous framework. These adsorption-desorption isotherms can also be utilized to estimate the pore size distribution and porosity of these films.

3:00pm **EL+AS+EM+MS+TF-ThA4 Mueller-Matrix Ellipsometry Studies of Chirality in Chitin-Based Structures and Thin Films of $Al_{1-x}In_xN$**, ***K. Järrendahl***, *H. Arwin, R. Magnusson, P. Sandström, C.-L. Hsiao, J. Landin, S. Valyukh, J. Birch*, Linköping University, Sweden

A limited number of natural structures are known to reflect light that has circular or near circular polarization. This is for instance, the case for some scarab beetles were it is suggested that the polarization is caused by chiral structures in the form of helicoids in the cuticles . In this study, Mueller-matrix spectroscopic ellipsometry is applied in the spectral range of 250 to 1000 nm to investigate optical response and structures of the cuticle of various scarab beetles of the Cetoniinae subfamily. We will present our measurements showing how the polarization changes with wavelength as well as incidence angle and specify the conditions for when the reflected light is circularly left- or right-polarized. In most cases the reflected light is left-polarized as described by negative values of the M41 Mueller matrix element. For *Cetonia aurata*, a green beetle with metallic appearance, this is clearly seen in a rather narrow spectral range (470-550 nm). For other beetles (*Potosia cuprea* and *Licola lugubris*) similar polarization behavior is observed but the polarization features occur in a broader spectral region. We will show that there are even beetles (e.g. *Plusiotis argentiola*) reflecting both left- (M41 < 0) and right-polarized light (M41 > 0) in different parts of the spectral region. The Mueller data, including observations of the degree of polarization, are used to obtain structural and optical parameters from model calculations.

Our attempts to fabricate artificial structures with similar polarization properties will also be presented. $Al_{1-x}In_xN$ thin films were grown on sapphire substrates by magnetron sputtering of indium and aluminum in a nitride atmosphere. Utilization of different seed layers and a substrate rotation gave chiral structures constituted by layers with a compositional gradient. Mueller-matrix results from these structures will be compared with the results from the natural structures. The Mueller data is also in this case very rich on information. In the initial steps to model these samples a similar approach as for the natural structures has been employed. Similarities and differences of the natural and artificial polarization response will be discussed in detail.

3:40pm **EL+AS+EM+MS+TF-ThA6 Mueller Polarimetry as a Tool for the Evaluation of the Diffraction Grating Profile Asymmetry**, ***T. Novikova***, *P. Bulkin,* LPICM, CNRS, Ecole Polytechnique, France*, V. Popov,* Moscow State University, Russia*, A. De Martino*, LPICM, CNRS, Ecole Polytechnique, France

Mueller polarimetry in conical diffraction has proved to be a powerful optical technique for the metrological characterization of diffraction gratings. It was already shown that the shape of grating profile can be successfully reconstructed via appropriate optical modeling using full Mueller matrix measurements [1]. We also demonstrated that this approach can be of particular interest in microelectronics technology for the detection of overlay errors, which frequently result from the alignment deficiencies in lithography [2]. In some cases the asymmetrical distortion of grating profile can be induced by the etch process, or even be intentional, like in blazed gratings fabrication. For these applications a technique that allows for fast non-contact evaluation of the profile asymmetry may be of great value.

We studied the Mueller matrix spectra of symmetrical [3] and asymmetrical photoresist diffraction gratings on chromium using MM16 spectroscopic polarimeter, commercially produced by Horiba Jobin-Yvon, in the most general geometry of conical diffraction. At this configuration the 0th order cross-polarization complex reflection coefficients are antisymmetrical ($r^0_{sp} = -r^0_{ps}$) , provided that the grating is composed of only reciprocal materials and is invariant under the rotation by 180° about the normal incidence [4]. It leads to the following relations between the elements of 2x2 off-diagonal blocks of Mueller matrix: $M_{ij} = \pm M_{ji}$.

The lack of rotational symmetry violates the electromagnetic reciprocity theorem for the 0th-order diffraction on the asymmetrical gratings and, consequently, breaks the symmetry of the off-diagonal blocks of Mueller matrix ($|M_{ij}|$ is not equal to $|M_{ji}|$). This property of Mueller matrix of asymmetrical gratings was experimentally observed and numerically modeled at any illumination condition with exception of planar and pure conical mounting. We showed that the non-reciprocity in diffraction gratings can be used for the unambiguous detection of the grating profile asymmetry. The optimal choice of measurement configuration, i.e. azimuthal and polar angles considerably increases the sensitivity of the above mentioned technique.

References:

[1] T. Novikova, A. De Martino, S. Ben Hatit, and B. Drévillon, Appl. Opt. **45**, 3688 (2006).

[2] T. Novikova, A. De Martino, R. Ossikovski and B. Drévillon, *Europ. Phys. J. Appl. Phys.* **31,** 63 (2005).

[3] T. Novikova, A. De Martino, P. Bulkin, Q. Nguyen, B. Drévillon, V. Popov, and A. Chumakov, *Opt. Express* **15**, 2033 (2007).

[4] L. Li, Opt. Soc. Am. A **17**, 881 (2000).

4:00pm **EL+AS+EM+MS+TF-ThA7 Monitoring Ultra-Thin Organic Film Growth, *In-Situ*, with Combined Quartz Crystal Microbalance and Spectroscopic Ellipsometry**, ***K.B. Rodenhausen**, B.A. Duensing, A.K. Pannier, M. Schubert,* University of Nebraska-Lincoln*, M. Solinsky,* The Procter & Gamble Company*, T.E. Tiwald*, J. A. Woollam Co., Inc.

We report a combinatorial approach to study ultra-thin organic films. This novel technique consists of *in-situ* spectroscopic ellipsometry and quartz crystal microbalance methods. In contrast to the quartz crystal microbalance, which is sensitive to the total mass attached to the surface, including the trapped solvent, spectroscopic ellipsometry only measures the amount of adsorbent on the surface. We also introduce a new "virtual separation approach" ($2\pi nd/\lambda \ll 1$) of analysis for the ellipsometry measurements. By using these two techniques in tandem, we are able to determine the thickness and solvent fraction of viscoelastic thin films.

We investigate cetyltrimethylammonium bromide (CTAB) thin films deposited onto a gold-coated quartz crystal as a model system. CTAB grown from a 2.5 mM solution demonstrates several phases in porosity evolution, including a temporary hold in water fraction as the film is rinsed off the substrate with water; these effects may be related to the structure of a CTAB bilayer.

In addition, a variety of self-assembled monolayers (SAMs) of alkanethiols on gold-coated quartz crystals are used as model biomaterials to determine the water fraction of an adsorbed prion layer. The porosity information distinguishes the proteins' conformation, dictated by the defined surface chemistries of the SAMs.

4:20pm **EL+AS+EM+MS+TF-ThA8 Ellipsometric Studies of Electronically Coupled PbSe and PbS Quantum Dot Thin Films**, ***S.G. Choi**,* National Renewable Energy Laboratory*, O.E. Semonin,* University of Colorado*, J.M. Luther, M.C. Beard, A.G. Norman,* National Renewable Energy Laboratory*, Z. Lin,* Colorado School of Mines*, A. Franceschetti,* National Renewable Energy Laboratory*, M.T. Lusk,* Colorado School of Mines*, A.J. Nozik*, National Renewable Energy Laboratory

Discovery of multiple exciton generation from colloidal suspensions of semiconductor quantum dots (QDs) has generated growing interests in realization of high-efficiency QD-based solar cells. Among a number of semiconductor QDs explored up to date, lead chalcogenides such as PbSe and PbS have been of great interest as a result of their wide tuning range of bandgap energy, abundance of materials, and large exciton Bohr radius.

In this presentation, I discuss optical properties of electronically coupled PbSe and PbS QD thin films. A series of QD multilayer thin films were prepared by a layer-by-layer dip-coating method onto glass substrates. Diameter of the QDs varies from 3.2 to 7.2 nm and from 3.5 to 8.3 nm for PbSe and PbS, respectively. Room-temperature pseudo-optical functions of the samples were measured by a rotating compensator-type, variable-angle spectroscopic ellipsometer. Transmittance data were also acquired in a normal-incidence configuration.

First, I determined refractive index $N = n + ik$ of the QD films using the B-spline basis functions within the multilayer model (ambient/surface roughness/QD film/substrate). We use the N obtained as the input parameters for modeling the internal quantum efficiency of the QD-based solar cell devices. Then, I extracted dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ for the ensemble of electronically coupled QDs using the Maxwell-Garnett effective medium approximations. The ε spectra show the first exciton peaks, and the E_1 and E_2 critical-point (CP) structures whose energies are higher than the corresponding bulk values probably due to the quantum confinement effects. This abstract is subject to government rights.

4:40pm **EL+AS+EM+MS+TF-ThA9 In-situ Temperature Measurements by Spectroscopic Ellipsometry: Application to a-Si based Thin Films**, ***D. Daineka**,* LPICM, CNRS, Ecole Polytechnique, France*, V. Suendo,* Institut Teknologi Bandung, Indonesia*, P. Roca i Cabarrocas*, LPICM, CNRS, Ecole Polytechnique, France

Accurate measurement of the substrate temperature is of crucial importance in many semiconductor technologies such as plasma enhanced chemical vapor deposition (PECVD). Traditional tools, both thermocouples and pyrometers, are not always reliable for in situ measurements in vacuum when the substrate can be out of thermal equilibrium. On the other hand, non-contacting optical methods allow to determine the surface temperature with great accuracy, provided the temperature dependence of optical constants for the studied material is known. Since recently, spectroscopic ellipsometers are widely available and often installed on the research deposition systems, which provides an opportunity to use them for temperature monitoring. We have studied the optical functions of amorphous silicon based thin films with spectroscopic ellipsometry in the temperature range from 290 to 520 K. The experimental data were modeled using Tauc-Lorentz dispersion law for amorphous materials. We have found that the temperature coefficients of Tauc-Lorentz parameters, such as the optical gap, are rather close for a few different materials. That similarity suggests that these values can be used to determine the surface temperature for a broad range of amorphous silicon based materials with a good accuracy. Practical examples of using spectroscopic ellipsometry for temperature measurements in the low pressure PECVD environment are given.

5:00pm **EL+AS+EM+MS+TF-ThA10 Real Time Spectroscopic Ellipsometry Studies of Amorphous and Nanocrystalline $Si_{1-x}Ge_x$:H Thin Films for Microbolometer Applications**, ***D.B. Saint John**, H.-B. Shin, M.-Y. Lee, E.C. Dickey, T.N. Jackson, N.J. Podraza*, Penn State University

Hydrogenated amorphous and nanocrystalline silicon (a/nc-Si:H), germanium (a/nc-Ge:H), and their alloys have been used and continue to be assessed for use in uncooled infrared microbolometer applications. These materials may be deposited as uniform layers using equipment common to the manufacturing of displays and photovoltaics and are thus more amenable to manufacturing considerations than the ion beam deposited vanadium oxide films used in most commercial microbolometers. Real optimization of material in the a/nc-$Si_{1-x}Ge_x$:H system for use in these devices requires a better understanding of the relationship between the key electrical properties of interest including resistivity (r), temperature coefficient of resistance (TCR), and the 1/f noise character as a function of the degree of order and composition of the films. $Si_{1-x}Ge_x$:H thin films were deposited using plasma enhanced chemical vapor deposition using SiH_4, GeH_4, and H_2 at variable H_2- dilution. These films have been monitored using in situ real time spectroscopic ellipsometry (RTSE) over a spectral range from 0.75 to 5.15 eV during deposition to detect changes in the film thickness and optical properties in the form of the complex dielectric function spectra ($e = e_1 + ie_2$) as a function of deposition time. From the RTSE measurements and analysis it is possible determine the structure of the material as amorphous, nanocrystalline, or mixed-phase and track the evolution of nanocrystallinity as a depth profile into the film. Ex situ Fourier transform infrared spectroscopic ellipsometry measurements over a spectral range from 0.05 to 0.75 eV were also performed to augment the complex dielectric function spectra and study absorption features relating to bonding. For electrical measurements, contacts were deposited in an isolated transfer length pattern for measurement of resistivity and TCR, while resistors with different volumes were made for volume normalization of the 1/f noise measurements. The TCR was measured from 20ºC to 55ºC. This study explores to correlations between the electrical and optical properties of a-$Si_{1-x}Ge_x$:H and nc-$Si_{1-x}Ge_x$:H as functions of film processing conditions, resultant composition, and order. a-$Si_{1-x}Ge_x$:H films were prepared as a function of germanium content and hydrogen dilution to identify the impact that germanium and improved order at higher hydrogen dilution conditions have on the electrical properties (r, TCR, 1/f noise). The impact on the electrical properties due to the incorporation of small fractions of nanocrystallites are explored using mixed-phase (a+nc)-Ge:H films with nanocrystallite profiles guided by depth profile studies.

5:20pm **EL+AS+EM+MS+TF-ThA11 Roll-to-Roll Fabrication of Thin Film Si:H Solar Cells: Real Time Monitoring and Post Deposition Mapping by Spectroscopic Ellipsometry**, ***L.R. Dahal**, Z. Huang, D. Attygalle, M.N. Sestak, C. Salupo, S.X. Marsillac, R.W. Collins*, University of Toledo

Real time spectroscopic ellipsometry (RTSE) has been used to monitor the roll-to-roll deposition of thin film Si:H n-i-p solar cells on flexible plastic substrates coated with a Ag/ZnO back-reflector. In this process, the RTSE monitoring position is located directly above the ZnO sputtering target (i.e., at the closest target-substrate separation). RTSE data collection is initiated before the plasma is ignited so that ZnO nucleation can be observed. The film thickness increases with time until a steady state is reached, after which the bulk layer thickness at the monitoring point is constant with time. This occurs when the elapsed deposition time equals the time required for the moving substrate to travel from the leading edge of the deposition zone to the monitoring point. Although a constant substrate speed is selected such that the final film thickness is achieved in the time required to move through the entire deposition zone, this speed does not allow study of film growth that occurs after the substrate passes the monitoring point. To solve this problem, the substrate speed is reduced only in the early stage of growth such that the final film thickness of interest is reached at the monitoring point. In this way, RTSE can be used to analyze the entire layer on an initial length of the roll before the full length of the roll is processed. The thickness evolution of ZnO in the case of both normal and reduced

speeds shows good agreement with a simple inverse square variation of the deposition flux from the target to the flexible substrate.

After cell deposition, spectroscopic ellipsometry (SE) has also been applied for large area mapping of the completed 15 cm wide roll, at up to 1.5 m long sections at a time. Key information such as critical point, oscillator amplitudes, band gap energies, and widths have been extracted from which material density, composition, grain structure, disorder, and defect density can be determined. In this paper, optical mapping was applied for the intrinsic absorber layer in a full device a-Si:H solar cell structure. The results clearly show the degree to which thickness uniformity of the absorber layer depends on the gas flow and the electrode configuration. Also, by parameterizing the optical functions of the intrinsic absorber layer using single Lorentz oscillator modified by a low energy absorption cut-off, a map of its band gap and oscillator width can be deduced. Such an SE application is ideal for evaluation of uniformity in bulk thickness db, surface roughness thickness ds, index of refraction, and extinction coefficient (n, k); the critical parameters for fabricating uniform and high efficiency solar modules.

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