Spectroscopic Ellipsometry Focus Topic
Room: 304 - Session EL+AS+BI+EM+SS-FrM

Application of SE for the Characterization of Organic and Biological Materials

Moderator: Tino Hofmann, University of Nebraska-Lincoln

8:20am **EL+AS+BI+EM+SS-FrM1 Multimodal Optical and Mass Spectrometric Imaging of Cells and Tissues**, ***DaeWon Moon***, DGIST, Republic of Korea **INVITED**

Understanding interfacial phenomena has been one of the main research issues not only in semiconductors but only in life sciences. I have been trying to meet the atomic scale surface and interface analysis challenges from semiconductor industries and furthermore to extend the application scope to biomedical areas. Optical imaing has been most widely and successfully used for biomedical imaging but complementary mass spectrometric imaging can provide more detailed molecular specific information

In this presentation, I report our recent activities of multimodal nanobio imaging of cardiovascular cells and tissues. Firstly, in atherosclerotic plaque imaging using coherent anti-stokes raman scattering (CARS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), multimodal CARS & SIMS analysis showed that increased cholesterol palmitate may contribute to the formation of a necrotic core by increasing cell death. Secondly, surface plasmon resonance imaging ellipsometry (SPRIE) was developed for cell biointerface imaging of cell adhesion, migration, and infiltration dynamics for HUVEC, CASMC, and T cells. SPRIE images were validated with confocal fluorescence microscopy. Collagen fibrils are widely used as cell adhesion substrates. Changes of surface composition and elastic modulus of collagen fibrils after thermal and acidic treatment were investigated by TOF-SIMS and non-contact force microscopy. Multimodal SPRIE & TOF-SIMS imaging would be a useful methodology for understanding cell-substrate interactions in tissue engineering.

In conclusions, multimodal optical and mass spectrometric imaging privides overall structural and morphological information with complementary molecular specific information, which can be a useful methodology for biomedical studies. Future challenges in optical and mass spectrometric imaging for new biomedical applications will be discussed regarding to in-vivo imaging.

9:00am **EL+AS+BI+EM+SS-FrM3 Sum Decomposition of Mueller Matrices from Beetle Cuticles**, ***Hans Arwin***, *R. Magnusson,* Linköping University, Sweden, *E. Garcia-Caurel, A. de Martino,* LPICM-CNRS, Ecole Polytechnique, France, *K. Järrendahl,* Linköping University, Sweden, *R. Ossikovski*, LPICM-CNRS, Ecole Polytechnique, France

Spectral Mueller matrices are very rich in information about physical properties of a sample. We have recently shown that polarizing properties like ellipticity and degree of polarization, can be extracted from a Mueller matrix measured on a beetle cuticle (exoskeleton). Mueller matrices can also be used in regression analysis to model nanostructures in cuticles. Here we present the use of sum decomposition of Mueller matrices from these depolarizing biological reflectors to explore the fundamental character of these reflectors. The objective is to decompose a Mueller matrix into well-defined ideal non-depolarizing matrices corresponding to mirrors, circular polarizers, halfwave retarders etc. Generally it is possible to decompose a measured depolarizing Mueller matrix M into four (or fewer) non-depolarizing matrices according to $\mathbf{M}=\alpha\mathbf{M}_1+\beta\mathbf{M}_2+\gamma\mathbf{M}_3+\delta\mathbf{M}_4$, where α, β, γ and δ are eigenvalues of the covariance matrix of **M**. Two strategies for decomposition will be discussed. A Cloude decomposition will provide the eigenvalues and also the $\mathbf{M}_i$'s although the latter will contain severe noise in some spectral regions. However, a major advantage with the Cloude decomposition is that the number of nonzero eigenvalues is directly obtained, i.e. the number of contributing $\mathbf{M}_i$ matrices. In an alternative decomposition, the $\mathbf{M}_i$'s are assumed and the eigenvalues are found by regression analysis based on **M**. In the case with two non-zero eigenvalues we define a model Mueller matrix $\mathbf{M}_D=\alpha_R\mathbf{M}_1+\beta_R\mathbf{M}_2$ with $\alpha_R+\beta_R=1$. With α_R as adjustable parameter, the Frobenius norm $||\mathbf{M}-\mathbf{M}_D||$ is minimized for each wavelength in the spectral range of **M**. For more complex structures, the regression can be extended by adding more matrices up to a total of four. Advantages with a regression approach are its simplicity and stability compared to a Cloude decomposition. The Mueller-matrix spectra of beetle cuticles are recorded with a dual rotating compensator ellipsometer in the spectral range 400 – 900 nm at angles of incidence in the range 20 - 75°. The application of decomposition on biological reflectors is demonstrated on **M** measured on the beetle *Cetonia aurata*, which represents a narrow-band chiral Bragg reflector with two non-zero eigenvalues. A decomposition in an ideal mirror and a circular polarizer is feasible. In another example, the broad-band and gold-colored beetle *Chrysina argenteola*, we show that more than two eigenvalues can be nonzero, especially at oblique incidence, and additional matrices are involved.

9:20am **EL+AS+BI+EM+SS-FrM4 Polymer- and Ceramic-Supported Hybrid Gas Separation Membranes Characterized by Ellipsometry**, ***Ioannis A. Mergos***, *H. Verweij*, The Ohio State University

Membrane structures consist of thin continuous layers deposited on porous ceramic or polymer supports. We have been developing inorganic and hybrid membranes for various applications that include gas separation (e.g. post-combustion CO_2 capture), water purification, Solid Oxide Fuel Cells (SOFC) and sensors. Spectroscopic Ellipsometry (SE) is a major non-destructive characterization tool, which can be used to obtain the thickness (typical range 50 nm…2 μm) and complex refractive index (n,k) of the supported membrane layers. This information, in turn, is used to obtain information about membrane composition, porosity and gas or water sorption. The characterization of fully-ceramic structures on optically smooth porous α-alumina surfaces (roughness ~25 nm, higher than most typical SE applications) has been employed by our group for several years. Recently we have expanded the use of SE to characterization of multi-layered membranes, and of inorganic or polymer layers on polymer supports, on coarser α alumina surfaces, and on ceramic tubes. Examples are γ- and α-alumina on polyethersulfone (PES) and poly-sulfone (PES), $Ce_{0.9}Gd_{0.9}O_{1.95}$ on tubular α-alumina, and successive layers of amorphous microporous silica and polydimethylsiloxane (PDMS) on mesoporous intermediate layers. We have achieved signal detection and interpretation to acquire meaningful results, even in multi-layered structures and in cases with substantial interfacial of surface roughness, or curvature. Overall, the application of SE, including non-destructive characterization at intermediate stages between deposition and processing steps, can significantly facilitate the design of gas separation membrane structures that combine organic and polymer layers.

9:40am **EL+AS+BI+EM+SS-FrM5 Spectroscopic Ellipsometry Methodology for Analysis of Thin Films with Significant Surface Non-idealities: Combining Through-the-Substrate and Film-Side Measurements**, ***Jian Li***, University of Toledo, *L. Mansfield,* National Renewable Energy Laboratory, *P. Pradhan,* University of Toledo, *H. Du, S. Glenn, J. Mann, A. Norman, K. Ramanathan,* National Renewable Energy Laboratory, *R.W. Collins,* University of Toledo, *G. Teeter, D. Levi*, National Renewable Energy Laboratory

Spectroscopic ellipsometry (SE) is a powerful tool for studying thin films, including the thickness and dielectric function, the latter being closely related to important properties such as composition, phase, grain size, porosity, and stress. The sub-nanometer sensitivity of SE is best exploited if all interfaces between layers, at substrate/layer and layer/ambient are abrupt and smooth. Even for the simple structure of substrate/film/ambient, however, whereby the film is fabricated in a uniform process, surface non-idealities including roughness, oxides, compositional variations, or a combination of these, are inevitable. If an accurate film dielectric function is of interest, then the widely-used effective medium approximation (EMA) treatment of the surface roughness can distort the result, especially in photon energy range of strong absorption.

In this work, an improved SE methodology has been developed, tested, and applied to study thin films with significant surface non-idealities. The investigated materials include $Cu(InGa)Se_2$, $Zn(O,S)$, Cu_2ZnSnS_4, and Cu_2SnS_3 deposited on transparent substrates by co-evaporation, sputtering, or chemical bath deposition. The film thicknesses in this study range from ~ 20 to 4000 nm, with potential applicability of the methodology over an even wider range. The key component of the SE methodology is integration of through-the-substrate (TS) SE with standard film-side (FS) SE. The following successes have been demonstrated.

(1) When the surface non-ideality is predominantly roughness within the EMA applicability, two-side (FS+TS) SE can minimize dielectric function distortion caused by the EMA assumptions.

(2) When the surface non-ideality is outside the EMA applicability and traditional SE methodology becomes unreliable, accurate results can be obtained using the FS+TS SE methodology, in which the dielectric functions of the surface and bulk layers can be allowed to vary wavelength by wavelength independently. Most thin films of this study fall into this category.

(3) When the surface is macroscopically rough and scatters light, films can be grown intentionally thick and hence rough enough to suppress specular

reflection from the surface. In this case, through-the-substrate SE alone can be used to extract the bulk film dielectric function.

An important criterion for evaluating SE analysis on semiconductor films is that the ε_2 spectrum should be flat and essentially zero below the band gap. It is demonstrated that the dielectric functions obtained through the above SE methodology either satisfy or better satisfy this criterion compared to previous studies. The limitations of the SE methodology will also be discussed.

10:00am **EL+AS+BI+EM+SS-FrM6 A Classical Model for Depolarization through Incoherent Superposition of Dipoles Driven by Evanescent Fields**, ***Kurt Hingerl***, University Linz, Austria

A finite spectral resolution and/or an imperfectly collimated beam /and or an (areal) extended light source / and or an (areal) extended detector and/ or a sample with a varying thickness can produce depolarization effects. However, despite these experimental findings, there are to our knowledge no physical models published which trace the origin of depolarization back to the atomic properties. Therefore, we explain depolarization by the following steps:

1) A mathematical model for cross- polarization: In structured samples the Fresnel reflectances are not correct any more, they rely on homogheneity (i.e. an arbitrary shift of the sample along any surface direction). Mathematicians are aware of this and the numerical tools developed by them, e.g. finite element methods (FEM) or rigorous coupled wave analysis (RCWA), take these effects into account, when matching boundary conditions. Mathematically the Jones matrix then possesses nondiagonal elements. This cross polarization signifies the presence of a totally polarized photon state, but takes into account that p- polarized incoming light creates s- polarized outgoing and vice versa.

2) Cross- polarization then has to take into account radiating dipoles, whose radiation create the scattered cross (and later, after incoherent superposition, partially de-) polarized field. In any structured sample there are inner boundaries present and it is straightforward to show that the usual boundary conditions on the continuity of the tangential electric field and the normal of the displacement field yield inherent contradictions at these inner boundaries. In order to fulfill the boundary conditions, close to the inner boundaries **evanescent fields** must be present, which drive the atomic dipoles in ***other spatial directions than the incoming field.***

3) Depolarization: The end point of the field of unpolarized light may be assumed to move quite irregularly, and the light shows no preferential directional properties when resolved in arbitrary orthogonal directions normal to the direction of propagation. Depolarization is mathematically described by the ***correlation*** which exists between these two orthogonal directions. Furthermore the extension of the light source, the extension of the detector and *the extension of the illuminated sample area* ***(especially its depth!)*** are reducing the value above. The measured intensity at the detector is obtained by the ***incoherent superposition*** of the single waves. The mathematical formulation is given by the Cittert- Zernike theorem (M. Born & E. Wolf, *Principles of Optics*, chapter X.9).

10:40am **EL+AS+BI+EM+SS-FrM8 The Development Of Highly-Oriented 3D Nanostructures For Use With Ultra-Thin Layer Chromatography And Ellipsometry**, ***Erika Pfaunmiller***, University of Nebraska Lincoln, *D. Peev, D. Sekora,* University of Nebraska-Lincoln, *S. Beeram,* University of Nebraska Lincoln, *C. Rice, M. Schubert, T. Hofmann, D. Hage*, University of Nebraska-Lincoln

Slanted columnar thin films based upon SiO_2 were deposited on glass substrates through the use of glancing angle deposition (GLAD). The typical length of these structures was between 500 nm and 2.5 μm. These thin films were then evaluated for use in ultra-thin layer chromatography (UTLC), which is a special type of thin layer chromatography (TLC) that uses supports that incorporate nanomaterials. In this work, a series of lipophilic dyes were analyzed through the use of both TLC and UTLC followed by detection through imaging ellipsometry. It has previously been demonstrated that changes in birefringence is seen as small organic molecules attach to some of the types of nanostructures that were used in this study. The principle behind the detection of organic chemicals that attach/adsorb onto such nanostructures is based on the variation of the optical anisotropy of highly-ordered 3D nanostructures with attached or adsorbed molecules. This causes screening of the dielectric displacement charges that are produced by the incident electromagnetic fields within the nanostructures, which can be measured as a variation of the effective birefringence of the highly-ordered 3D nanostructures. Measurement of this birefringence was done through generalized imaging ellipsometry. This combined imaging and separation approach should be useful for label-free detection in UTLC and for the chromatographic analysis of a various target compounds.

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