

# Thursday Morning, November 3, 2011

## Spectroscopic Ellipsometry Focus Topic

Room: 209 - Session EL+AS+EM+MS+PS+TF-ThM

## Spectroscopic Ellipsometry of Biological Materials and Organic Films

**Moderator:** M. Creatore, Eindhoven University of Technology, the Netherlands, K.G. Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **EL+AS+EM+MS+PS+TF-ThM1 Application of Various Spectroscopic Ellipsometry Techniques for In Situ Studies of Thin Polymer Films on Solid Substrates, K.-J. Eichhorn,** Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**

Thin films of functional polymers are not only widely integrated into modern micro- and nanoelectronic devices, but also used to modify solid surfaces for biosensor, biomedical and antifouling applications.

Therefore, in the first part I will report on improved temperature-dependent spectroscopic Vis-ellipsometry experiments to study confinement effects on the polymer dynamics in thin films to address a question which is controversially discussed in the polymer physics community for a long time past: Is there really a significant change of the glass transition temperature  $T_g$  of polymers when confined in nanoscopic films (studied here down to about 10 nm thickness)? We compared well-known linear polystyrenes of different molecular weights /1/ and hyperbranched polyesters having different architectures and functional groups /2/. Films of different thickness were prepared by spin-coating on silicon wafers, carefully equilibrated and measured in dependence on temperature (up to 250°C) in an inert gas atmosphere. The  $T_g$  data were determined from the ellipsometric results and discussed.

In the second part, "smart" surfaces will be presented which can be used for controlled adsorption and release of biomolecules. For that, different types of stimuli-responsive polymer brushes were prepared on solid substrates by a "grafting-to" procedure. The brush properties (e.g. swelling/collapsing) as well as the resulting adsorption/desorption of model proteins (e.g. Human Serum Albumin, Chymotrypsin) can be switched in an appropriate aqueous medium with temperature (PNIPAAm) and/or pH (PAA-P2VP). The corresponding processes at the solid-liquid interface were studied in-situ by spectroscopic Vis- and IR-ellipsometry /3,4/.

/1/ M. Tress, M. Erber, E.U. Mapesa, H. Huth, J. Müller, A. Sergei, C. Schick, K.-J. Eichhorn, B. Voit, F. Kremer, *Macromolecules* 43 (2010), 9937-9944

/2/ M. Erber, A. Khalyavina, K.-J. Eichhorn, B. Voit, *Polymer* 51 (2010), 129-135

/3/ E. Bittrich, M. Kuntzsch, K.-J. Eichhorn, P. Uhlmann, J. Polym. Sci. B, *Polym. Phys.* 48 (2010), 1606-1615

/4/ Y. Mikhailova, L. Ionov, J. Rappich, M. Gensch, N. Esser, S. Minko, K.-J. Eichhorn, M. Stamm, K. Hinrichs, *Anal. Chem.* 79 (2007) 20, 7676-7682

8:40am **EL+AS+EM+MS+PS+TF-ThM3 Hard Matter Meets Thin Polymer Films-Spectroscopic Ellipsometry as a Versatile Tool to Investigate Properties of Responsive Poly(N-isopropylacrylamide) Systems with Incorporated Magnetic Nanoparticles, S. Rauch,** Leibniz-Institut für Polymerforschung Dresden e. V., Germany

Responsive polymer systems designed by using polymer brushes or hydrogels are interesting systems, which can exhibit reversible or irreversible changes in their physical and structural properties to special environmental conditions (e.g. temperature or magnetic fields). The temperature responsive poly(*N*-isopropylacrylamide) (PNIPAAm) is one of such polymers. It undergoes a phase transition in aqueous solution at its lower critical solution temperature (LCST) of 32 °C which induces an increase in hydrophobicity. Combined with the properties of magnetic nanoparticles (NP) (e.g.  $Fe_3O_4$  or  $CoFe_2O_4$ ) these systems can lead to new surface functionalities with new interesting properties for many applications, as sensing, wettability or (bio)adhesion.

For the design of such thin film systems a basic knowledge of the film characteristics is essential. Therefore it is first necessary to know how many nanoparticles are inside or attached to the system. By using spectroscopic Vis-Ellipsometry (SE) it is not only possible to investigate optical properties of these films but also the composition of it, e.g. volume fraction of  $Fe_3O_4$ -NP.

We studied two types of films and present results for a thin NP-composite film prepared by pre-mixing of the PNIPAAm with hydrophobic  $Fe_3O_4$ -NP, spin-coated and grafted to a silicon substrate (System 1) and a film prepared by adsorption of hydrophilic functionalized  $Fe_3O_4$ -NP onto PNIPAAm brushes (System 2). The former system was chosen to develop an optical model starting from a simple two component effective-medium-approach (Maxwell-Garnett-EMA) using the optical constants of the pure polymer measured by SE and of  $Fe_3O_4$  with averaged data taken from three different publications. The SE best fit-results were validated against scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

After transferring this optical model to System 2, the adsorption of hydrophilic functionalized  $Fe_3O_4$ -NP onto PNIPAAm brushes was investigated and will be discussed with additional results obtained from contact angle (CA) and phase transition (LCST) measurements.

9:00am **EL+AS+EM+MS+PS+TF-ThM4 The White Scarab Beetle *Cyphochilus insulanus* –Scattering and Polarization Properties, C. Akerlind,** Swedish Defence Research Agency / Linköping University, Sweden, H. Arwin, Linköping University, Sweden, T. Hallberg, H. Kariis, Swedish Defence Research Agency, Sweden, J. Landin, K. Järrendahl, Linköping University, Sweden

Three methods were used to characterize the optical properties of the light scattering white scarab beetle *Cyphochilus insulanus*. Spectral directional hemispherical (DH) reflectance measurements in the wavelength region 250 nm to 25  $\mu$ m were performed using integrating spheres. The general spectral appearance shows a relatively strong reflectance band in the range 400 - 1600 nm. The Bidirectional Reflection Distribution Function (BRDF) was measured over a semi-circle in the plane of incidence at the wavelengths 633 nm and 3.39  $\mu$ m, using s- and p-polarized light. In the visible the BRDF data shows a near Lambertian behaviour with a constant BRDF for most angles, i.e. the light is diffusely scattered. For large incident angles and in the infrared the BRDF is more specular. Full Mueller-matrix spectroscopic ellipsometry (MMSE) measurements were performed in the wavelength range 250 - 1000 nm at angles of incidence between 45° and 75° using a dual rotating compensator ellipsometer. The Mueller data show that the reflected light in general has a high degree of polarization  $P$  even for nonpolarized incident light. The angular dependence of  $P$  was pronounced for incident p-polarized light and was very low near the Brewster angle. In comparison,  $P$  was high for all measured angles for incident s-polarized light. Close to the Brewster angle, the reflected light showed a high ellipticity for incident p-polarized light. The optical data is used to model the structure and optical response of the beetle cuticle. With input from the DH and BRDF-data analysis of the Mueller Matrix data was made using Fresnel-based layer modelling. 2-, 3- and n-phase models are compared. The obtained optical properties are also used to calculate color data in terms of chromaticity and whiteness. The scattering properties of the *Cyphochilus insulanus* cuticle are also discussed by combining the BRDF and MMSE data as well as recently obtained Mueller matrix imaging polarimetry results.

9:20am **EL+AS+EM+MS+PS+TF-ThM5 Real-time Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipative Characterization of Biomolecule Adsorption within Sculptured Thin Films, T. Kasputis, D. Schmidt, K.B. Rodenhausen, H. Wang, A.K. Pannier, M. Schubert,** University of Nebraska - Lincoln

Recent improvements in nanofabrication strategies have led to the development of precisely crafted nanostructures with intricate features. Incorporating biomolecules such as proteins, DNA, drugs, and even whole cells could allow for functionalization of nanostructured surfaces for biological applications including biosensing, tissue engineering scaffolds, and drug and gene delivery. Along with the nanofabrication of biological devices, there is a need to develop instrumentation capable of probing and characterizing the dynamic evolution of these bio-functionalized interfaces. Spectroscopic ellipsometry combined with quartz crystal microbalance with dissipation (SE/QCM-D) is a non-destructive optical/mechanical characterization technique that reveals dynamic properties, including average film thickness (with sub-angstrom resolution), adsorbed mass, and porosity.

Nanostructures in the form of sculptured thin films (STF) were fabricated by glancing angle deposition via electron beam evaporation of titanium onto gold-coated quartz sensors. The sensors were then mounted within an SE/QCM-D liquid cell, and proteins of varying sizes were deposited and characterized, *in-situ*. Protein adsorption was detected shortly after introducing the protein solutions by SE and QCM-D as a change in the optical response and decrease of vibration frequency, respectively. QCM-D reported greater adsorbed mass for larger proteins (fibronectin) than smaller

proteins (bovine serum albumin). The adsorbed mass of proteins within the nanostructured scaffold exceeded that of proteins on flat surfaces, confirming that the STFs are capable of trapping proteins. Analysis of the anisotropic optical response from the nanostructures, which is very sensitive to environmental changes, adds complementary information on protein adsorption; the optical quantification is in agreement with QCM-D results. In addition, the adsorption of other biomolecules, such as cells and DNA complexes, has also been accomplished. The use of combinatorial SE/QCM-D to characterize and monitor the attachment of biomolecules on complex nanotopographies will improve the design and fabrication strategies for a wide array of biotechnological devices.

9:40am **EL+AS+EM+MS+PS+TF-ThM6 Characterization of Multilayer Organic Thin Film for Use as an Aptamer Biosensor with Hybrid Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation**, *J.Y. Gerasimov, K.B. Rodenhausen, H. Wang, R.Y. Lai, M. Schubert*, University of Nebraska - Lincoln

DNA aptamer molecules passivated by alkanethiols can be used for biological detection and screening. Through the use of spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, selective binding of analytes to chemisorbed aptamer probes can be observed *in-situ*. The system analyzed consists of a gold-coated quartz substrate, a multilayer organic thin film (containing aptamer probe, alkanethiol, and single-stranded DNA analyte), and physiological buffer solution. The attachment and detachment of material, the hybridization efficiency of the aptamer probes, and changes in the porosity of the multilayer organic thin film were all determined by SE/QCM-D.

In this contribution, we present the real-time SE/QCM-D characterization of (a) the formation of the aptamer probe layer, (b) the subsequent chemisorption of alkanethiol, and (c) the interrogation of single-stranded DNA that is non-complementary or complementary to the sequence found on the aptamer probe. The aptamer DNA sequence encodes codon 12 of the *K-ras* gene; mutations of this gene are frequently found among pancreatic cancer patients. We found that introduction of either complementary or non-complementary DNA caused increases of the multilayer organic thin film thickness. However, our SE/QCM-D analysis showed that the porosity of the multilayer organic thin film responded differently depending on the compatibility of the DNA analyte. The SE/QCM-D technique provides evidence for different surface attachment mechanisms and can be useful in characterizing biological interfaces.

10:40am **EL+AS+EM+MS+PS+TF-ThM9 Contamination Processes of EUV Optics Characterized by Spectroscopic Ellipsometry**, *L.J. Richter, C. Tarrío, S. Grantham, S.B. Hill, T.B. Lucatorto*, National Institute of Standards and Technology, *N.S. Faradzhev*, University of Virginia

Extreme ultraviolet (EUV) lithography using 13.5 nm light is emerging as a viable tool for semiconductor fabrication at design rules below 32 nm. Tool performance critically depends on limiting and mitigating degradation of the EUV optical elements. A primary degradation mechanism is the EUV induced deposition of carbon from ambient species originating from outgassing of the unbaked vacuum system and/or outgassing from the EUV irradiation of the resist. Using the high brightness of the Synchrotron Ultraviolet Radiation Facility (SURF-III) at NIST both fundamental studies of EUV induced contamination and practical ("witness plate") studies of resist out gassing are performed. Typical deposits are hydrogenated amorphous carbon features with peak thicknesses of about 1 nm and nominal lateral extent of 1  $\mu$ m. Both ex-situ, small spot mapping spectroscopic ellipsometry (SE) and in situ single-wavelength imaging nulling-ellipsometry are used for rapid, sensitive, contamination metrology. Fundamental studies of contamination by admitted gases indicate that the process is a complex function of both gas pressure and photon dose. Correlations between SE and XPS are suggestive that, at high EUV fluxes, densification can occur resulting in spatial variation in the deposit dielectric function. The use of principal component analysis of the SE images to highlight the spatial diversity will be discussed.

11:00am **EL+AS+EM+MS+PS+TF-ThM10 Characterization of Organic Solar Cells Materials and Structures by Spectroscopic Ellipsometry**, *J.P. Piel, L. Kitzinger, A. Bondaz, C. Defranoux*, SEMILAB-SOPRALAB, France

Spectroscopic Ellipsometry (S.E) is a well known optical technique widely used for the characterisation of all types of thin films for determination of film thickness and optical indices on glass or plastic substrates.

S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.

We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately and fully characterized from their absorption bands in the visible and UV range (190nm to 900nm).

Transmission and absorption can be also measured at the same time and be used to determine the optical properties of these materials.

Using these refractive indices, analysis of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation Q inside an organic solar cell composed of a thin film stack. We present an example performed on a single cell and on a tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure their optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi-layer stacks, through encapsulated samples, from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the efficiency of the thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrodes by S.E. and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Akerlind, C.: EL+AS+EM+MS+PS+TF-ThM4, **1**  
Arwin, H.: EL+AS+EM+MS+PS+TF-ThM4, 1

## — B —

Bondaz, A.: EL+AS+EM+MS+PS+TF-ThM10, 2

## — D —

Defranoux, C.: EL+AS+EM+MS+PS+TF-ThM10, **2**

## — E —

Eichhorn, K.-J.: EL+AS+EM+MS+PS+TF-ThM1, **1**

## — F —

Faradzhev, N.S.: EL+AS+EM+MS+PS+TF-ThM9, **2**

## — G —

Gerasimov, J.Y.: EL+AS+EM+MS+PS+TF-ThM6, **2**

Grantham, S.: EL+AS+EM+MS+PS+TF-ThM9, 2

## — H —

Hallberg, T.: EL+AS+EM+MS+PS+TF-ThM4, 1  
Hill, S.B.: EL+AS+EM+MS+PS+TF-ThM9, 2

## — J —

Järrendahl, K.: EL+AS+EM+MS+PS+TF-ThM4, 1

## — K —

Kariis, H.: EL+AS+EM+MS+PS+TF-ThM4, 1  
Kasputis, T.: EL+AS+EM+MS+PS+TF-ThM5, 1  
Kitzinger, L.: EL+AS+EM+MS+PS+TF-ThM10, **2**

## — L —

Lai, R.Y.: EL+AS+EM+MS+PS+TF-ThM6, 2  
Landin, J.: EL+AS+EM+MS+PS+TF-ThM4, 1  
Lucatoro, T.B.: EL+AS+EM+MS+PS+TF-ThM9, **2**

## — P —

Pannier, A.K.: EL+AS+EM+MS+PS+TF-ThM5, 1  
Piel, J.P.: EL+AS+EM+MS+PS+TF-ThM10, 2

## — R —

Rauch, S.: EL+AS+EM+MS+PS+TF-ThM3, **1**  
Richter, L.J.: EL+AS+EM+MS+PS+TF-ThM9, **2**  
Rodenhausen, K.B.: EL+AS+EM+MS+PS+TF-ThM5, **1**; EL+AS+EM+MS+PS+TF-ThM6, 2

## — S —

Schmidt, D.: EL+AS+EM+MS+PS+TF-ThM5, 1  
Schubert, M.: EL+AS+EM+MS+PS+TF-ThM5, 1;  
EL+AS+EM+MS+PS+TF-ThM6, 2

## — T —

Tarrio, C.: EL+AS+EM+MS+PS+TF-ThM9, 2

## — W —

Wang, H.: EL+AS+EM+MS+PS+TF-ThM5, 1;  
EL+AS+EM+MS+PS+TF-ThM6, 2