A classical model for depolarization by temporal and spatial decoherence

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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 in any ellipsometric or polarization measurement. 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, in the talk I will explain crosspolarization - and subsequently depolarization by considering the ***common- not separable-*** effect between the light beam and the sample, described by **coherence length and coherence area**.
For inhomogeneous samples with dimensions smaller than the coherence area, the fields have to be added coherently. However, inner and non-planar boundaries give rise to evanescent fields in the vicinity of these boundaries. Parallel and perpendicular field components oscillate and decay differently in the vicinity of the boundaries, therefore cross- polarization (incident s- polarized light excites reflected p-polarized light and vice versa) occurs.[1] In inhomogeneous samples the Fresnel reflectances are not correct any more, these strictly rely on homogeneity (i.e. arbitrary shifts of the sample along any surface direction change the measurement).

However, in optics we never measure the electric fields, because our available detectors are much too slow, but we measure their ***statistical*** second moments. In homogeneous samples with thick transparent overlayers it turns out that depolarization arises through the temporal decoherence of photons, and the measured Müller matrix (MM) elements are given by a convolution of the spectral width of the light source and a sample property: the thickness of the transparent overlayer.

For inhomogeneous samples, when the sample sizes or structures are larger than the coherence area, then the different local polarization states in reflection coming from different materials have to be added incoherently- partially depolarized light results.[2] Also here the measured Müller matrix is given by a convolution of a light source property (i.e. the coherence area) and a sample property: the structure size). For both depolarization mechanisms mathematical models[3] will be presented, allowing to predict the polarization response, i.e. all MM elements for periodic structures, metamaterials and thick films.

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[2] The mathematical formulations- which will be largely avoided in the talk- are given through the coherency matrix / respectively the Stokes vectors, and decoherence shows up by the Cittert- Zernike theorem (M. Born & E. Wolf, *Principles of Optics*, chapter X.9).

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INFRARED SPECTROSCOPIC ELLIPSOMETRY OF SiO_2 TRAPEZOIDS AND BIOHYBRID SiO_2/PROTEIN INTERFACES

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Infrared spectroscopic ellipsometry yields in-situ information about the micrometer-sized surface structure and surface chemistry of components relevant for solar cells, LEDs, biotemplates and biosensors. While ellipsometric scatterometry is already established in the UV/VIS spectral range for the integrated circuit industry, our approach combines the investigation of micrometer-sized periodic structures with the analysis of molecular vibrations [1, 2].

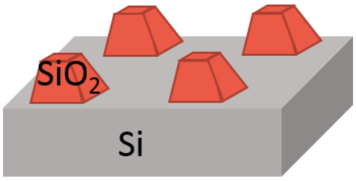

Fig. 1. Sketch of SiO_2 trapezoids

We measured the Mueller matrices of trapezoidal SiO_2 columns on Si with periods from 10 to 20 μm in both lateral directions (Fig. 1.). The modeling by Rigorous Coupled Wave Analysis shows good agreement for two different azimuth angles of sample rotation and geometrical lengths which correspond to SEM results. Moreover, simulations suggest that the off-diagonal Müller matrix elements are especially sensitive to variations of the azimuth angles and the trapezoidal baseline length.

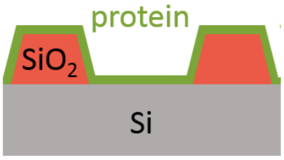

Fig. 2. Cross section of protein coated SiO_2 stripes

To describe a system with a biohybrid interface, micrometer-sized lamellar SiO_2 gratings were produced on Si and coated with a nanometer-thin monolayer of human serum albumin (HSA, protein, Fig. 2.). The infrared ellipsometric spectra were recorded before and after the protein coating. The comparison of the spectra shows geometrical characteristics as well as protein related vibrational peaks which, in principle, can elucidate the secondary protein structure.

Keywords: Infrared Ellipsometry; Scatterometry; Mueller Matrix; Biohybrid Interface

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ULTRA-THIN POLYMERS OF INTRINSIC MICROPOROSITY IN FLUIDS

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Polymers of Intrinsic Microporosity (PIMs) are widely regarded as having the potential to revolutionize such fields as molecular separations, catalysis or energy storage [1]. PIMs possess high microporosity often with pores similar to sizes of small gas molecules (3 – 6 Å) that enable effective “sieving” of gases and vapors. Such a structure forms naturally as a result of PIMs extremely rigid backbones that pack inefficiently in a solid state following deposition from a polymer solution. The easy processing of PIMs allows their introduction on a large industrial scale using the existing manufacturing facilities.

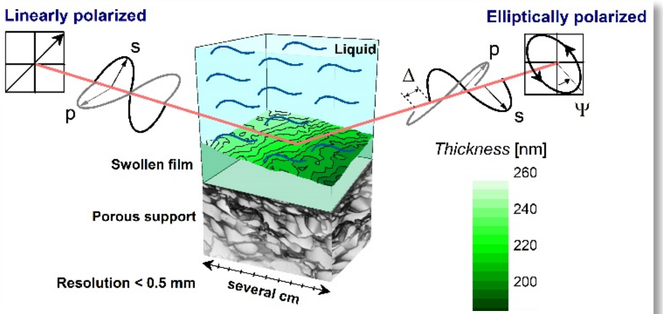

Figure 1 In-situ spectroscopic ellipsometry applied to directly image thin film composite

In this contribution, *in-situ* interference-enhanced ellipsometry is used to characterize ultra-thin (down to 6-7 nm) PIMs interacting with a variety of fundamentally and technologically important fluids including high pressure gases, liquids or vapors [2–4]. Next to characterization of thin PIM films ellipsometry is applied to study thin film composite membranes consisting of a selective skin deposited on a porous substrate [5]. Such geometry, highly unusual in typical ellipsometry analysis, mimics an actual highly efficient membrane that could be used in a large scale molecular separation plant.

Keywords: Polymers of Intrinsic Microporosity; In-situ Ellipsometry; Industrial Membranes

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ELLIPSOMETRY OF THIN PEPTIDE FILMS

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Spectroscopic ellipsometry is increasingly used for investigation of biofilms and biological materials because of its non-invasive manner. In the case of biofilms, the investigated material might be present on the surface only in small amounts forming an island-like coating. In this work, we used various types of peptides which adhesion differences in the case of deposition to n- and p-type silicon were determined in [1]. We investigate the applicability of different ellipsometric models for such peptide films. We also present which models lead to unphysical result and how it is possible to choose the correct ones utilizing only ellipsometric measurements.

Three different approaches were built to model our peptide films: i) a perfect layer which optical properties are modeled with Sellmeier-dispersion, ii) Sellmeier-dispersion extended with Gaussian absorption, iii) Sellmeier-dispersion assuming a non-continuous layer. Although the peptides are transparent in the visible spectral range as supported by absorption measurements, the first model failed. The second and the third approaches described the measured data with almost the same fitting quality, although their physical background is completely different. The second model applies a perfect layer with a slight absorption, and the third deals with a transparent layer which does not cover the substrate perfectly. To resolve this contradiction the results of a simulation will be presented that show the compatibility of the last two models, and explain why both models can describe the measured data. We will show that the absorption obtained in the second model can originate from the discontinuity of the layer. According to theory and simulations, the patterned character of the layer should lead to depolarization, which could ease the finding of the correct model [2].

However, in most cases depolarization is an undesired feature since it deteriorates degree of polarization, limiting the applicability of classical models. Therefore, through the examples of different sample types we emphasize the importance of handling depolarization in general [3,4].

Keywords: Peptide; Depolarization; Patterned layer ellipsometric model

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Please indicate preferred presentation:

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SPECTROSCOPIC ELLIPSOMETRY CHARACTERIZATION OF HYBRIDIZATION OF DNA ON GOLD SURFACES

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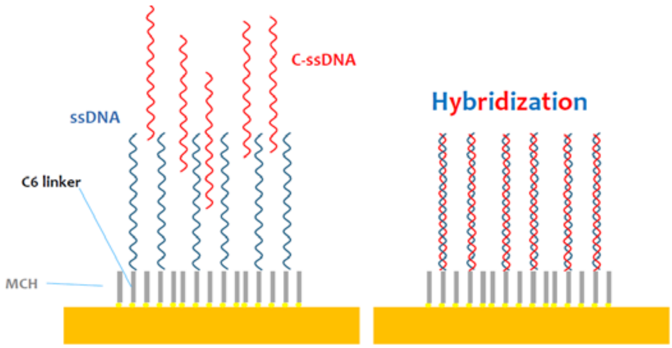

We recently coupled Spectroscopic Ellipsometry (SE) and AFM nanolithography methods to investigate the bonding of biomolecules at gold surfaces functionalized with well-organized compact thiolate Self-Assembled Monolayers (SAMs). AFM nanolithography was employed in so-called nano-shaving and nano-grafting modes [1,2] allowing precise determination of height of SAMs, which is important to feed the SE analysis. We present SE results (in-liquid and ex-situ) on a system of importance in the design of biosensors. Experiments on single-stranded ss-DNA were devoted to the detection of specific bonding through hybridization with complementary strands (c-DNA). The SE analysis of the precursor SAM, performed through the difference spectra method, allowed to disentangle the spectral features characteristic of the ss-DNA molecules and the molecule-surface bond. In particular a strong absorption in the UV range (260-270 nm) was detected in both in-situ and ex-situ data which was reproduced by a multi-oscillator model, consistently with known spectral response of DNA basis. The SE analysis with difference spectra was also able to clearly detect the hybridization process in mixed SAMs of ssDNA with mercaptohexanol (MCH), a short thiolate molecule which, through interaction with the C6 linker of ss-DNA (see cartoon) favors a standing-up organization of ss-DNA on the surface, in turn helping Hybridization. The influence of Hybridization on SE spectra turned out to be equivalent to a thickness increase of the film, which was confirmed by AFM nanoshaving. Control experiments performed by exposing the precursor ss-DNA layer to non-complementary DNA strands revealed no spectral change at all.

Keywords: Spectroscopic ellipsometry, DNA, bio-sensors

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Determination of the glass transition region of PVME by means of spectroscopic ellipsometry

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In this presentation, we report on the determination of the glass transition temperature of thin layers of Polyvinylmethylether (PVME) depending on the thickness of the polymer layer. The glass transition of thin polymer layers is currently under much investigation due to the nano-confinement effects proposed to appear in dependence on the layer thicknesses in the nm range. The properties of the polymer, the temperature range, as well as the thicknesses range of the polymer layers pose a serious challenge to the investigation by means of spectroscopic ellipsometry. By careful choice of experimental parameters, we were able to investigate the thickness change by temperature of PVME layers in the range between 2 and 300 nm and in the temperature range between 200 K and 340 K. By optimizing the analysis process, we were able to determine T_g values within this parameter range with sufficient accuracy to investigate the T_g change due to confinement effects.

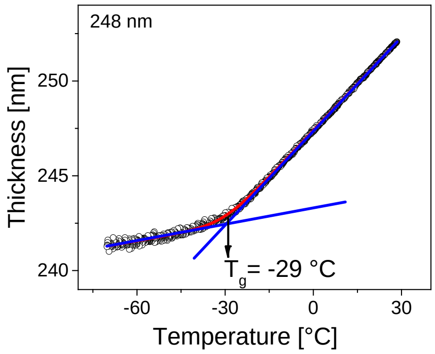

Fig. 1. T_g determination of a PVME layer

Alongside the change of position of the glass transition with thickness, we discuss the details of the ellipsometric analysis and its implications for the resulting thermal properties of the thin polymer layers [1] as well as the accuracy of the T_g value with respect to the method used in the analysis process.

Keywords: Polymers, PVME, temperature dependent ellipsometry, glass transition

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GRAPHENE FUNCTIONALIZED BY ULTRA-THIN ANCHOR LAYERS TOWARDS BIOSENSOR APPLICATION

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The functionalization of single layer graphene with specifically binding receptor molecules enables the facile fabrication of biosensors. The linkage between graphene and the receptor can be easily achieved by covalently bound molecules. We present the deposition of ultra-thin layers of such linker molecules on large area CVD-grown graphene by the electrochemical reduction of aryl diazonium salts containing amino, maleimide or thiol groups.[1] The successful deposition of the functional groups and the change of the graphene structure were detected by infrared spectroscopic ellipsometry, Raman backscattering, and electrochemical quartz crystal microbalance measurements. The homogeneity of the about 4.5 nm thin electrochemically prepared functional layer was verified by infrared atomic force microscopy.[2] The reactivity of these functional groups was tested by specific wet-chemical modification with small molecules via amidation reaction including immobilization of COOH-modified quantum dots. Finally, the functionalized and modified graphene was transferred from copper to different substrates including glass, silicon and flexible PTFE tape.

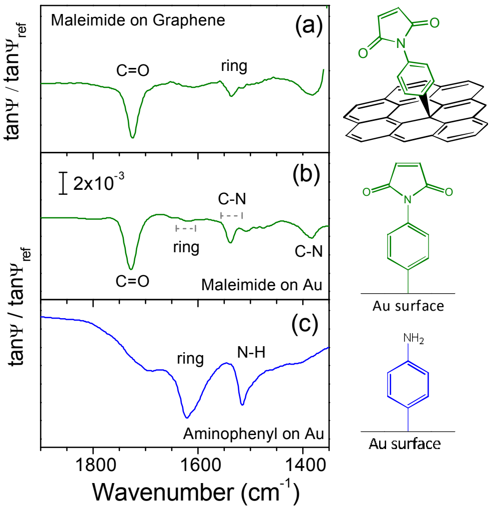

Fig. 1: IRSE spectra of Graphene (a) and Au (b,c) surfaces functionalized by maleimide (a,b) or amino (c) groups.

Keywords: Surface functionalization, biosensing, infrared-spectroscopic ellipsometry

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ZWITTERIONIC POLYMER SURFACES BASED ON PHOSPHORYLCHOLINE: SWELLING AND BIOMOLECULE INTERACTION

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Zwitterionic polymers with positively and negatively charged molecular groups along the chains are showing excellent biocompatibility and are promising for applications in implant medicines, biosensors, or drug release [1]. Of special interest are coatings based on the zwitterionic phospholipid polymer poly (2-methacryloyloxyethyl phosphorylcholine) (PMPC) due to their biomimetic resemblance of phospholipid bilayers in biomembranes [2].

We prepared MPC – containing polymer layers based on the statistical copolymer MPC-*co*-GMA (Fig. 1a) with different layer thicknesses and analyzed their swelling behavior, protein resistance and phospholipid interaction by in-situ VIS-ellipsometry. We found good resistance to the adsorption of bovine serum albumin (BSA), the most abundant protein in the blood plasma, and considerable adsorption of the phospholipid DPPC (lipid for cell membrane models) (Fig. 1b).

Additionally, we mixed the MPC with the pH-sensitive polymer poly acrylic acid (PAA) aiming at stimuli-responsive blend layers with anti-fouling properties.

Ellipsometric investigations were combined with surface characterization by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measurements, as well as quartz crystal microbalance (QCMD) analysis.

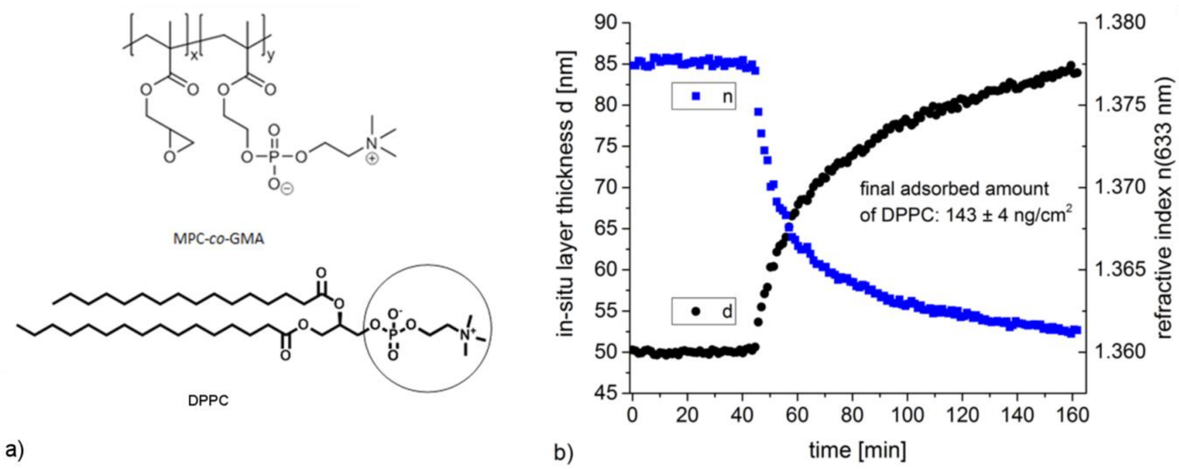

Fig. 1: a) Chemical structures of MPC-*co*-GMA (top) and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) (bottom), b) in-situ layer thickness and refractive index at λ=633 nm for DPPC adsorption ($c^{DPPC}_{in\text{-}solution}$ = 0.25 mg/ml) to a MPC-*co*-GMA layer (dry thickness: 15 nm) in 10 mM sodium phosphate buffer solution at pH 5.8 with 1 mM $CaCl_2$.

Keywords: phosphorylcholine; in-situ VIS ellipsometry; protein adsorption

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