The depolarization in granular media: a Mueller matrix approach

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We describe a general method to disclose the information hidden in Mueller matrices experimentally obtained from depolarizing samples. Although spectroscopic Mueller-matrix ellipsometry allows for a model-free characterization of inhomogeneous samples, i.e., independently from any assumption on the sample structure, the interpretation of the obtained results is often challenging. The proposed method combines three different decomposition techniques applied to the measured Mueller matrices in transmission and reflection of granular thin films with different thicknesses and densities. We demonstrate that the comparative analysis of the respective differential-, product-, and sum-decomposition of the Mueller matrices, together with correlation effects and the visualization as a Poincaré sphere, reveals the particular underlying physical processes of depolarization. As an example, we apply this method on granular BaSO4 thin films. This method is general and can be applied to a wide variety of intrinsically inhomogeneous materials with applications in physics, industry, biology, or medicine.

QUANTIFYING UNCERTAINTIES OF RECONSTRUCTED PARAMETERS IN OPTICAL SCATTEROMETRY OF NANOSTRUCTURED SURFACES

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Methods for solving Maxwell's equations in three spatial dimensions are an integral part of many optical metrology and ellipsometry setups in technology and science. In critical dimension metrology characterising deviations and uncertainties from (idealised) targets accurately play an important role.

We discuss a method which allows to efficiently compute highly accurate solutions and parameter sensitivities to Maxwell's equations for general scattering targets. The method is based on hp-adaptive finite-elements. Therefore, complex shapes including corner roundings and sidewall angles can be handled without additional computation cost compared to the idealized case of geometries composed from rectangular shapes. We present a combination of machine learning tools and Newton-like methods to solve the inverse problem and quantify parameter uncertainties.

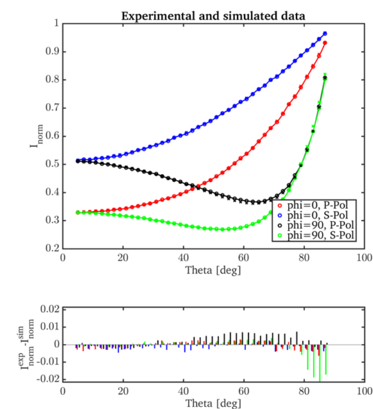

Fig. 1. Experimental and simulated data for a reconstructed line grating with corner roundings and non-rectangular sidewalls

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Keywords: Electromagnetic field solver; finite elements, uncertainty quantification; Bayesian optimization, optical metrology

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AZIMUTH-DEPENDENT OPTICAL ANISOTROPY AT THE EDGES OF MICROSTRUCTURES

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The comprehensive characterization of nanometer thickness microstructures is extremely important and in urgent demands in the area of nanoscience and nanotechnology, particularly for the micro/nano devices. Tremendous optical microscopes were developed for the microstructure characterization including ellipsometric microscope, near-field ellipsometric microscope, differential confocal microscope, scanning optical interfermeter and reflectance difference microscope (RDM). [1] Among them, RDM is a simple and convenient method while possessing the advantages of high optical anisotropy sensitivity, non-destructive and rapid response. Besides, the normal incident light of RDM greatly simplifies the data analysis. [1, 2] Two reasons mainly contribute to the optical anisotropy at the edges of step microstructures. Firstly, the light scattering induced by the tilt edge of step structure, inevitably at process of manufacture, breaks the cylindrical symmetry of the normally incident light and leads to an optical anisotropy signal. Secondly, the discontinuity at the boundary of two different materials composed surface introduces a phase difference between the two halves of the light spot and gives rise to an optical anisotropy signal too. [3] In most cases, it is hard to discriminate the two reasons when the lateral length of the edge of step structure is smaller than the lateral resolution of measurement method. Therefore, ”false” anisotropy signals are probably introduced into the real signals, such as non-uniformity of the sample surface and misalignment of components of instrument setup, which demands rigid challenge for RDM instrumentation.

Here, we present a new type of azimuthal dependence reflectance anisotropy microscopy (ADRDM) based on liquid crystal retarder to meet this urgent challenge. [4] An in-situ and online calibration method was developed to eliminate the testing errors introduced by the asymmetry of the optical system. Using our proposed ADRDM, we directly and precisely image the optical anisotropy at edges of microstructures and demonstrate its polarization-dependence feature.

Keywords: Microstructures; Reflectance difference microscope; Polarization-dependence

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ROUGH CIGS SURFACE ANALYZED WITH RAYLEIGH-RICE THEORY

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We employ Müller matrix ellipsometry to study the high efficiency thin film photovoltaic material copper indium gallium selenide Cu(In,Ga)Se_2 (CIGS) [1]. The analysis is complicated by a surface roughness with an rms value of 68 nm, measured with confocal microscopy. We use Rayleigh-Rice (RR) theory [2] to take the optical effect of this surface roughness into account. The roughness parameters σ (rms height of roughness) and ξ (roughness correlation length) are found from the Müller parameters by comparing them to calculations based on RR theory for a library of structures. Figure 1 shows the measured data and the optimal calculated solution.

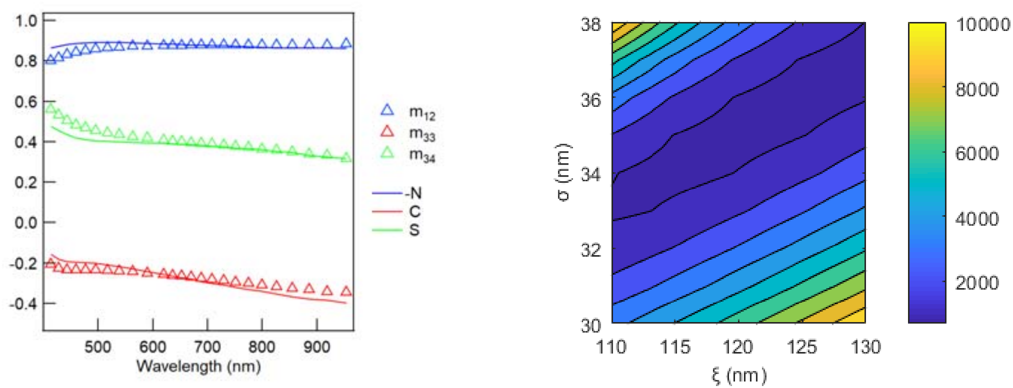

Figure 1. Left: Experimental Müller matrix elements (m_{12}, m_{33}, and m_{34}) and best calculated solution (N, C, and S) corresponding to σ = 36 nm and ξ = 125 nm. Right: Error χ^2 of comparison between experimental data and model as function of the roughness parameters σ and ξ.

The roughness parameters extracted from the analysis are comparable to values found using confocal microscopy and AFM, showing that the Rayleigh-Rice model can be employed to account for roughness effects in ellipsometric measurements. We investigate if the difference between the methods could be due to the fact that ellipsometry is more sensitive to high spatial frequency roughness than low frequency components. We find that the observed ellipsometry sensitivity is almost independently of the spatial frequencies of the roughness.

Keywords: Müller matrix ellipsometry, Copper Indium Gallium Selenide, Rayleigh-Rice theory

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Spectroscopic ellipsometry for the determination of thickness and porosity of mesoporous metal oxide films

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Thin mesoporous metal oxide films are versatile and attractive candidates for several energy applications like photovoltaics, electrolysis or batteries. Due to their high surface area and ordered pore structure, mesoporous metal oxides demonstrate higher activities. The performance of the porous films is affected by properties like size and shape of the mesopores as well as the crystallinity of the framework. The exact determination and metrological evaluation of the complex morphology of thin mesoporous films requires a new analytical approach employing combined data from different analytical techniques.

In this contribution we present an evaluation procedure based on spectroscopic ellipsometry (SE) to analyze thin mesoporous iridium oxide films. Mesoporous IrO_2 films were prepared via dip-coating from a solution containing a triblock-copolymer and an iridium precursor in ethanol.[1] Deposited films were calcined in air at temperatures between 300 and 600 °C. Their morphology was studied with SEM and electron probe microanalysis (EPMA)[2] and correlated to SE using the Bruggeman effective medium approach (BEMA)[3]. Figure 1a shows a top-view SEM image of mesoporous IrO_2 film calcined at 375 °C. The image reveals that the films exhibit a well-ordered mesopore structure. Figure 1b is a parity plot of film thicknesses determined by cross-section SEM versus SE of IrO_2 film samples prepared at different calcination temperatures. The porosity from the SE model is in good agreement to the porosity values obtained by EPMA (Fig. 1c).

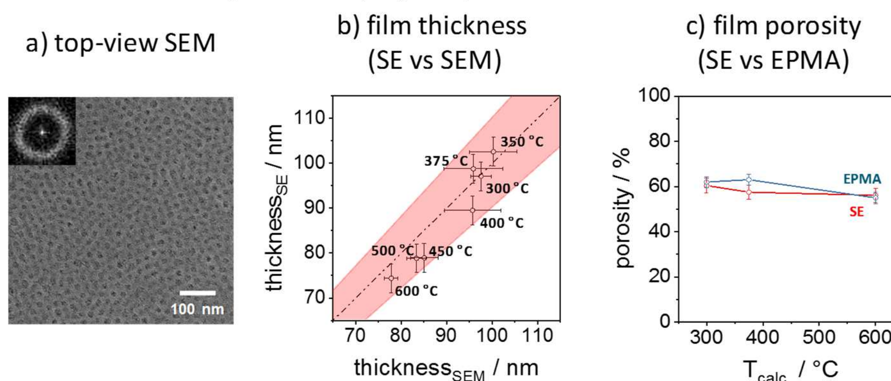

Figure 1: Characterization of mesoporous IrOx thin films via scanning electron microscopy (SEM), spectroscopic ellipsometry (SE) and electron probe microanalysis (EPMA).

The contribution will assess in detail the novel approach to analyses the morphology and porosity of thin metal oxide films. Moreover, the facility of a multi-sample analysis, the sensitivity analysis as well as the mapping of samples will be discussed.

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ANISOTROPY OF THIN FILMS AND AGGREGATES BY IR NANOPOLARIMETRY

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Resolving anisotropy at the nanoscale requires new spectroscopic methods overcoming the diffraction limit with high sensitivity to both the in- and out-of-plane optical properties of the sample. IR nanopolarimetry transfers the classical approach to the nanoscale by combining AFM-IR with polarized QCL sources (Fig. 1) [1]. The method uses an AFM tip to directly probe IR absorption via thermal expansion of the sample under p- and s-polarized low-power QCL pulses in ambient conditions allowing for straightforward spectra-structure correlations [2].

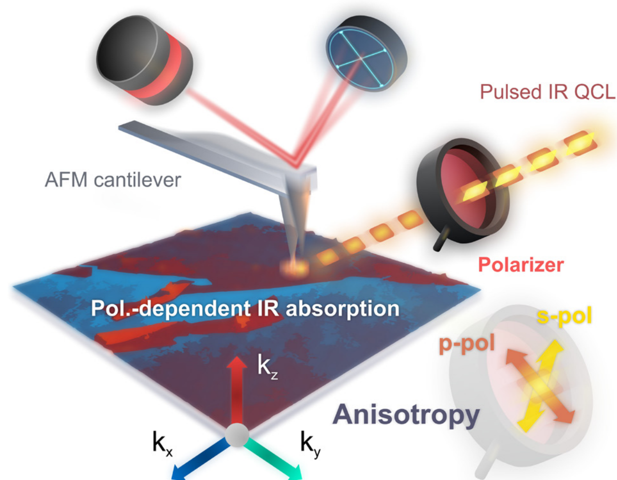

Fig. 1. Schematic of the AFM-IR nanopolarimetric setup in reflection geometry accessing in- and out-of-plane molecular anisotropy via polarization-dependent sample absorption

IR nanopolarimetry provides insights into anisotropy of thin films, surfaces, and aggregates including composition, interactions, molecular orientation, and oscillator strength induced phenomena with ≤ 30 nm spatial resolution in seconds [1–3].

This presentation will highlight the broad applicability of the method to polymer science, (bio)macromolecular research, and IR nanophotonics by focusing on the following applications: anisotropy of layered thin polyimide films [1], ordering mechanisms of supramolecular porphyrin aggregates [2], oriented protein aggregation upon adsorption [1], polaritonic modes in thin silica films [3], and polarization-dependent biosensing of a peptide nucleic acid [4] on modified graphene films [5].

The analysis of the nanoscale anisotropy is supported by vibrational and electrodynamic calculations [1].

Keywords: Nanopolarimetry; AFM-IR; Anisotropy; Molecular orientation; Light–matter interactions; Spectra-structure correlations; Thin films; Aggregates; Polymers; Proteins; Oxides; Polaritons

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Imaging Mueller-Matrix Ellipsometry of Anisotropic Thin-Film Semiconductors

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Imaging Mueller-Matrix Ellipsometry (IMME) extends the powerful technique of Mueller-Matrix measurements into the world of microstructured samples, reaching lateral resolutions that are beyond the limits of conventional non-imaging ellipsometers. Here, we present applications of IMME for the quantitative optical analysis of microstructured anisotropic thin-film layers of semiconducting materials.

Few-layer black phosphorus features exceptional anisotropic optical and electronic properties making it an interesting option for research on 2D-semiconductors for electronic devices [1, 2]. We carried out optical measurements of the orientations and the optical dispersion of the in-plane principal axes of microscopic, mechanically exfoliated flakes of black phosphorus by means of IMME.

Thin-film crystallites of the semiconducting organic material Thiophene-phenylene were grown by a solvent-based self-assembly technique on a silicon substrate. Ellipsometric contrast micrographs revealed a vast variety of different domains on the examined sample that correspond to different layer thicknesses forming a terracelike structure (Fig.1). Rotational IMME scans of the sample yielded the in-plane orientation of the crystallites' optical axes. Combined with spectroscopic measurements, the dispersion function of Thiophene-phenylene and the terraces' layer thicknesses were obtained.

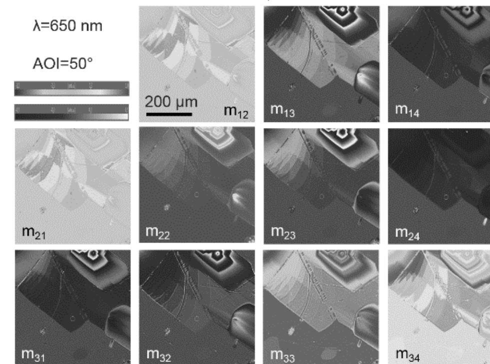

Fig. 1. 3x4-Mueller-Matrix micrographs of Thiophene-phenylene crystallites

Keywords: Mueller Matrix; Imaging Ellipsometry; 2D materials; organic semiconductors; anisotropy

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Ellipsometric Micromapping of Graphene grown on Copper-foil

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The demand of high quality graphene e.g. for electronic applications raised the necessity for the direct growth of Graphene on Cu-foils [1]. To investigate the layer structure and coverage of Graphene, conventional methods are SEM or optical microscopy after oxidizing the foil. SEM requires high vacuum and is not suitable for the detection of defects, layer number and uniformity on large areas. To investigate Graphene with optical microscopy the foil either needs to be oxidized, hence destroyed, or the Graphene needs to be transferred to suitable substrates, e.g. Si/SiO_2.

In the talk we present, imaging ellipsometry is able to characterize the Graphene directly grown on the foil. Besides the plethora of optical properties, the combination of microscopy and ellipsometry reveals foldings of the Graphene on the Copper-foil. These foldings are induced by the different cooling coefficients of Graphene and Cu. An automatic height alignment across the whole Copper-foil allows to measure Δ and Ψ micromaps of the creased foil. The automatic stitching of all measured field of views yield to a map of Δ and Ψ of the complete sample with a lateral resolution of 4 µm (Fig.1). In [2] a flakesearch algorithm is presented, that allows the localization of regions with defined layer numbers. The algorithm is extended to pinpoint monolayer regions on the complete map of Δ and Ψ and calculate the coverage. Measuring micromaps of Δ and Ψ offers a microscopic insight to the lateral distribution of Copper-oxide layer thickness even underneath a Graphene crystallite.

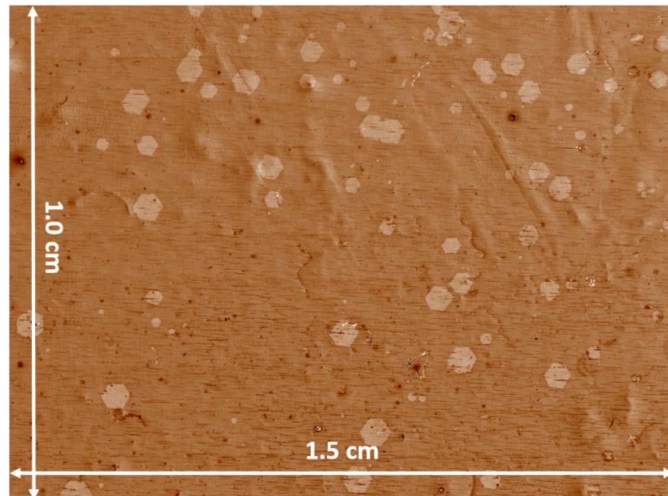

Fig. 1. Complete Δ map of Graphene on Cupper

Summing up, we will present cutting-edge technology for the characterization of Graphene directly grown on Cupper-foil including a detailed description of the substrate copper-oxide layer, altogether with the highest lateral resolution in the lower µm range.

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Keywords: Graphene; Copper-foils; Imaging Ellipsometry

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FAST DETECTION OF WATER NANOPOCKETS UNDERNEATH WET-TRANSFERRED GRAPHENE

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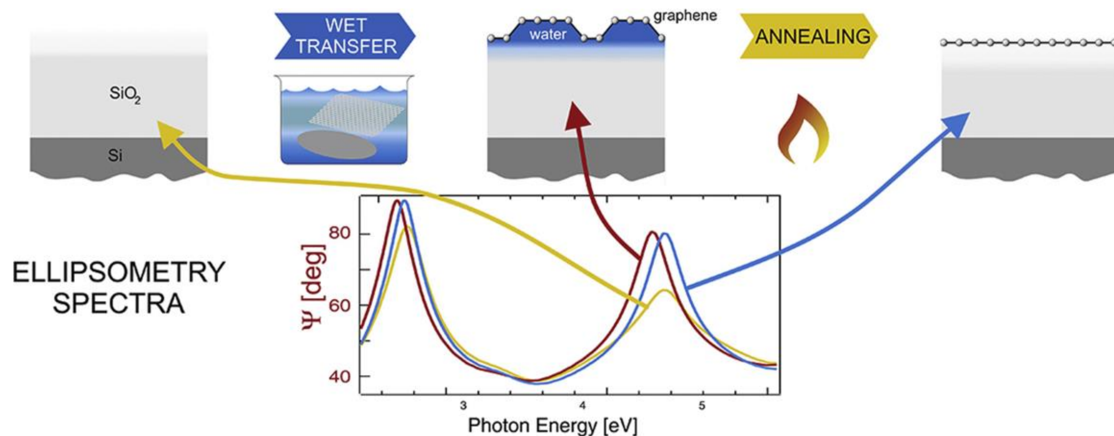

We report an investigation of the graphene/substrate interface morphology in large-area polycrystalline graphene grown by chemical-vapour deposition and wet-transferred onto Si wafers. We combined spectroscopic ellipsometry, X-ray photoelectron spectroscopy and atomic-force microscopy in order to yield morphological and chemical information about the system. The data showed that wet-transferred samples may randomly exhibit nanosized relief patterns indicative of small water nanopockets trapped between graphene and the underlying substrate. These pockets affect the adhesion of graphene to the substrate, but can be efficiently removed upon a mild annealing in high vacuum. We show that ellipsometry is capable of successfully and reliably detecting, via multilayer dielectric modelling, both the presence of such a spurious intercalation layer and its removal [1]. The fast, broadly applicable and noninvasive character of this technique can therefore promote its application for quickly and reliably assessing the degree of adhesion of graphene transferred onto target substrates, either for ex-post evaluation or in-line process monitoring.

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Keywords: Spectroscopic ellipsometry, graphene, annealing

ELLIPSOMETRIC IMAGING OF LOW-CONTRAST SURFACE MODIFICATIONS AND DEPOLARIZATION CONTRAST IMAGING (DCI) OF PARTICULATE ACCUMULATIONS

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Imaging of surfaces regarding topographical, morphological, micro-structural, and chemical features is a key requirement for quality control for the identification of contaminated, degraded, damaged or deliberately modified surface areas vs. clean, virgin, undamaged or unmodified regions. As optical functions may represent any of these changes on the micro- and nano-scale, imaging ellipsometry (IE) is the technique of choice using either intensity, phase, or/and amplitude contrast for visualization of low-contrast surface modifications [1, 2].

Defects or surface and film features whether native or artificial, intended or unintended, avoidable or unavoidable as well as surface pattern are of interest for quality control. In contrast to microscopic techniques operated at normal incidence, ellipsometry as oblique-incidence technique provides improved contrast for vertically nano-scaled add-on or sub-off features such as ultra-thin transparent films, metallic island films, carbon-based thin films, laser modification or laser induced damage, dried stain, cleaning agent or polymeric residue.

Two-sample reference techniques, i.e. referenced spectroscopic ellipsometry (RSE) may further increase sensitivity and decrease measurement time. In case of particulate accumulations depolarization contrast imaging (DCI) may improve the lateral resolution beyond the Abbe limit. This has been proven for silica spheres as reference in terms of single particles, particulate accumulations or particulate mono-layers and layer stacks. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used for reference measurements of particle diameter, particle height, or particulate layer/accumulation thickness.

It has been shown that single silica particles of 250 nm in diameter, i.e. at least a factor of 4 better than the lateral resolution limit as of now, can be *visualized* on even substrates. However, the ellipsometric *measurement* of particle diameters of this size needs further efforts interpretation.

Keywords: low-contrast surface modifications; particulate distributions; imaging ellipsometry(IE) and depolarization contrast imaging (DCI)

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