



Bundesanstalt für
Materialforschung
und -prüfung

HyMET Workshop on optical surface analysis methods for nanostructured layers, preliminary program



Date: Thursday, Oct 10, 2019

Venue: BAM Adlershof building 8.05 lecture hall and meeting rooms

- 09:00 – 09:10: Opening: Andreas Hertwig
- 09:10 – 10:30 Session 1, Chair:
- 09:10 – 09:30: 1. Talk: Dan Hodoroaba (BAM)
- 09:30 – 09:50: 2. Talk: Omar El Gawhary (VSL)
- 10:10 – 10:30: 3. Talk: Cornelia Streeck (PTB)
- 10:30 – 10:50: 4. Talk: Lidija Matjacic (NPL)
- 10:50 – 11:10: Coffee break
- 11:10 – 12:30 Session 2, Chair:
- 11:10 – 11:30: 1. Talk: Emmanuel Nolot (CEA / LETI)
- 11:30 – 11:50: 2. Talk: René Sachse (BAM / TUB)
- 11:50 – 11:10: 3. Talk: Peter Thiesen (Accurion)
- 12:10 – 12:30: 4. Talk: Miroslav Valtr (CMI)
- 12:30 – 15:00: Lunch break, poster session, exhibition



All participants welcome. There is no admission fee, but you have to register via mail to:

thin-films@bam.de

Session 1: 1. Talk

New nanoparticle reference material candidates for traceable size and shape measurement from EMPIR project nPSize

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New model nanoparticles with well-controlled shape were synthesized within the EMPIR project nPSize - Improved traceability chain of nanoparticle size measurements. Their systematic characterization takes place by the traceable methods scanning/transmission electron microscopy, atomic force microscopy and small angle X-ray scattering. Following reference nanoparticle candidates are under investigation with respect to their homogeneity and stability: titania nanoplatelets (10-15 nm x 50-100 nm), titania bipyramides (~60 nm x 40 nm), titania acicular particles (100 nm x 15-20 nm; aspect ratio 5.5/6), gold nanorods (~10 nm x 30 nm), and gold nanocubes (~55 nm x 55 nm x 55 nm).



Session 1: 2. Talk

Measuring nano-dimensions by light

Omar El Gawhary¹ and Petro Sonin¹

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Our society is experiencing a unique progress which can be ultimately traced back to the ability of current technologies to control matter at dimensional scales previously inaccessible. Since nothing can be reliably produced if it cannot be, equally reliably, measured and characterized, optical measurements techniques have played a key role in such progress by developing tools to measure geometries and some of the physical properties of those products with high precision, accuracy and the required spatial resolution. More importantly, optical measurement methods have also turned out to be very convenient from a practical viewpoint because they are fast, non-invasive, and have proper penetration depth in matter: all crucial features that determined their success and dissemination within the academia and the industry.

In this talk we will discuss the current and future development of optical scatterometry (OS) and will present a hybrid system that integrates single wavelength OS with high resolution ptychography, which is a method especially suited to measure phase objects. Finally, we will present our current research on multiwavelength coherent scatterometry and how that can help face some of the challenges that optical metrology is expected to address in the near future.



Session 1: 3. Talk

Characterization of advanced materials at the nano- and microscales by X-ray spectrometry using calibrated instrumentation

Burkhard Beckhoff¹, Philipp Hönicke¹, Yves Kayser¹, Florian Peinl¹, Christian Stadelhoff¹, Cornelia Streeck¹, Rainer Unterumsberger¹, André Wählich¹, Jan Weser¹, Claudia Zech¹

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The development of new materials and the assessment of nanomaterials require the correlation of the materials' functionality or toxicity with their chemical and physical properties. To probe these properties, analytical methods that are both sensitive and selective at the nano- and microscales are required. The reliability of most analytical methods is based on the availability of reference materials or calibration samples, the spatial elemental composition of which is as similar as possible to the matrix of the specimens of interest. However, there is a drastic lack of reference materials in particular at the nanoscale. PTB addresses this challenge by means of a bottom-up X-ray analytical method where all instrumental and experimental parameters are determined with known contributions to the uncertainty of the analytical results. This first-principle based approach does not require any reference materials but a complete characterization of the analytical instruments' characteristics and, in addition, of the X-ray fundamental parameters related to the elements composing the sample. X-ray spectrometric methods allow for the variation of the analytical sensitivity, selectivity, and information depth needed to effectively reveal the spatial, elemental, and chemical specimen parameters of interest. Examples of particle characterization, interfacial speciation, elemental depth profiling, as well as layer composition and thickness characterizations in advanced materials will be given. Recent instrumental achievements provide access to beam profiles in the nanometer range to qualify heterogeneous



materials as well as towards the operando speciation of nanoscaled battery materials. X-ray spectrometry under grazing incidence is capable to reveal analytical and dimensional information from layered systems and particles deposited on surfaces.

Session 1: 4. Talk

Material characterization with ion beams

Lidija Matjačić¹

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The use of charged particles in material science is based on their surface and near-surface interaction with the matter. Ion beams cover a wide energy range and are thus not restricted to accelerators only. The ion-solid interaction results with many different events which depend on the energy of the impinging particles and these are recoil of the nuclei, transmission and scattering of particles, generation of X-rays, γ -rays, recoiled atoms and material ejection. Material modification is a well-established area of research ensuing from some of these events which is an important tool used in material engineering. Material characterization is obtained using a set of analysis techniques known as the ion beam analysis (IBA). Most of these techniques tackle the elemental composition and, perhaps the chemical state. However, secondary ion mass spectrometry (SIMS) enables the molecular analysis and can provide molecular structure, depth profiling and chemical mapping of inorganic and organic materials. Different IBA techniques can be combined and, in case of the accelerators, performed simultaneously using the same instrument and as such offer advantageous complementary information about the material. Ion beams are particularly used in the semiconductor industry with the purpose of the manufacturing and providing insight into the stability, performance and degradation. In this talk, examples of using high- and low-energy beams in material characterization will be shown. Former include Rutherford Backscattering Spectrometry (RBS) in the analysis of Si single crystal implanted with As and Particle Induced X-ray Emission (PIXE) in the analysis of chalcogenide PV materials.



The latter comprises Time-of-Flight SIMS (ToF-SIMS) in the analysis of halide perovskite solar cells, controlling the Cu-catalyzed graphene nucleation and analysis of MOS devices.

Session 2: 1. Talk

Instrumental setup and calibration methodology of in-fab spectroscopic ellipsometry tools and their impact on the accuracy of the optical constants of thin layered materials

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Spectroscopic ellipsometry is extensively used in fabs and research and technology organizations to characterize and monitor the thickness and the optical property of thin layered materials. Whereas sub-nanometer (resp. few thousandths) accuracy in thickness (resp. refractive index) is often claimed, one should keep in mind that this analysis relies on tools, which characteristics may vary significantly from one site to another or even within one fab. Differences in the spectral range or in the instrumental function (spectral bandwidth, angular spread) must be taken into account in the data reduction process in order to minimize tool-related uncertainties. In addition, the calibration strategy does have a significant influence on the ability of spectroscopic ellipsometry to reveal small process-induced variability. This paper will first discuss about tool-induced uncertainty in spectroscopic ellipsometry, and will then show how in-fab ellipsometry can benefit from the high accuracy of M-line spectroscopy by virtue of dedicated calibration strategy.



Session 2: 2. Talk

Spectroscopic ellipsometric analysis of elemental composition and porosity of mesoporous iridium-titanium mixed oxide thin films for electrocatalytic splitting of water

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Porous materials play an important role in several fields of technology, especially for energy applications like photovoltaics, electrolysis or batteries. The activity of porous films is affected by properties like porosity, film thickness, chemical composition of the material as well as the crystallinity of the framework. The complex morphology of such porous films constitutes a challenge for modern analytical techniques and requires approaches employing the combination/complementation of data of different analytical methods. In this contribution we characterize thin mesoporous iridium-titanium mixed oxide film properties by spectroscopic ellipsometry (SE).

The thin films were analyzed with SE using the Bruggeman effective medium approximation (BEMA) for modelling. The results were compared with electron probe microanalysis (EPMA) as part of a combined SEM/EDS/STRATAGEM analysis. The SE model includes the IrOx-TiOx material and the EMA modeled porosity with a void fill factor. The IrOx-TiOx material consists itself by an EMA model for the mixture of iridium oxide and titanium oxide.

The contribution assesses in detail the advantages and limitations of the spectroscopic ellipsometry analysis for the porosity as well as the for the composition of thin metal



oxide films. Moreover, the comparison with other measurement techniques and the combination of datasets from multiple measurements are discussed.

Session 2: 3. Talk

Imaging Ellipsometry: Thin Film Metrology with Microscopic Lateral Resolution in the Field of New Materials for Energy Applications

Peter Thiesen¹ and Stefan Schneider¹

¹ Accurion GmbH, Göttingen, Germany

The combination of imaging from microscopy (magnified microstructures) with the sensitivity for thin films from ellipsometry (<0.1 nm – 10 μm thickness), makes imaging ellipsometry (IE) a powerful method to characterize thinnest microscopic layers and micro structured materials. For example, the technique allows to measure monolayers of 2D-materials, but also to visualize these monolayers on arbitrary substrates. Microscopic maps of Δ/Ψ can be recorded for different wavelength to obtain hyperspectral datasets. Microscopic maps, revealing lateral variations of optical properties and thicknesses, are the major advantage of imaging ellipsometry. In addition, large areas can be scanned and recorded maps can be stitched to create a single map of Δ/Ψ to determine e.g. coverage and layer thicknesses distribution of samples that are larger than the field of views.

In the talk we are going to use innovative materials for energy application to display the entire range of methods that can be performed with a spectroscopic imaging ellipsometer. The talk will also include the latest developments of this technique: Imaging ellipsometry in the UV down to 190 nm and microscopic thin-film metrology on curved surfaces. Regarding former camera techniques, the limitation for imaging ellipsometry to 250 nm was literally written in stone in the past. Since new UV cameras and polarization optics are now commercially available, it is possible to overcome this limitation. Another general limitation in ellipsometry was the layer-thickness of thin films



on curved surfaces. In order to overcome this limitation, Accurion developed a generalized approach for the calculation of the Mueller-Matrix of a tilted isotropic sample. We apply our model in order to extract the sample parameters N, C, S (or equivalently Δ and Ψ) from the Mueller-Matrix measured on a strongly tilted or curved, but otherwise isotropic sample.

The summary should be the starting point for a fruitful discussion about imaging ellipsometry focusing on optical surface analyzing methods for nanostructured layers.

Session 2: 4. Talk

Characterization of nanocomposite films by spectroscopic imaging reflectometry

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During the past decades nanocomposite polymer coatings have attracted increasing attention because of their unique optical, mechanical, magnetic and optoelectronic properties arising from the combination of organic matrix and inorganic nanoparticles. Spectroscopic imaging reflectometry is a method for optical characterization of samples. It can be used to e.g. map thickness inhomogeneities of a thin film. Contrary to a classical, non-imaging, reflectometer this device features high lateral resolution and it is fast.

In our contribution, we focused on optical characterization of amorphous $\text{SiO}_x\text{C}_y\text{H}_z$ composite films deposited by radio frequency (13.56 MHz) plasma-enhanced chemical vapor deposition operated under dusty plasma conditions. Hybrid metrology aspects, i.e. combination of different characterization techniques such as imaging reflectometry, large area atomic force microscopy or scanning thermal microscopy, will also be addressed.