Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C1

Optical Metrology in Design, Optimization, and Production of Multifunctional Materials

Moderators: Ludvik Martinu, Polytechnique Montreal, Nikolas Podraza, University of Toledo

8:00am **C1-1 Metamaterials: from Design and Modeling to the Experimental Confirmation of their Optical Performance***, **Michel Lequime**,* Institut Fresnel, France **INVITED**

Control of the microstructure of the matter at the sub-wavelength scale offers a great flexibility for designing artificial materials with an exotic electromagnetic response at optical frequencies, like for instance, the near-zero or negative index of refraction. The optical properties of such new, artificial materials (usually called meta-materials) are derived both from the inherent properties of their constitutive elements as well as the geometrical arrangement of these elements. Their development paves the way for controlling and manipulating light through entirely new schemes (slow light, perfect lens ...).

Numerous examples of such metamaterials including fishnet structures and metasurfaces will be provided. Manufacturing techniques, such as electron-beam lithography, focused ion-beam milling or interference lithography will be described, as well as the characterization methods including refraction measurements, spectral transmittance and reflectance measurements, interferometric measurements.

Possible applications to thin-films and multilayer stacks will be analyzed in a preliminary way.

8:40am **C1-3 Use of FDTD Method for Data Analysis of Spectroscopic Ellipsometry Data of Non-periodic sub-wavelength Structures***, **Juan Antonio Zapien**,* City University of Hong Kong, Hong Kong*; Y Foo,* City University of Hong Kong, Hong Kong Special Administrative Region of China

The optical response of complex, non-planar samples have the capability to determine superb sub-wavelength imaging information based on spectroscopic ellipsometry (SE), non-imaging, measurement and full vectorial data analysis. This has played a vital role in optical critical dimension (OCD) characterisation for the semiconductor industry. Rigorous coupled-wave analysis (RCWA) sets the standard in the determination of the fine structure of 1D gratings based on polarimetric and scattering techniques [1]. The ability to reproduce that level of detail in the characterization of complex nanostructured samples, particularly 2D or plasmonic nanostructures, is yet to be demonstrated using RCWA and is also much needed for sensing, active metamaterials research, and others [2,3]. To date, the use of RCWA analysis for such complex structures is largely limited to quantitative modeling of reflectance ratios whereas phase information, crucial for enhanced sensing capabilities [3], is largely disregarded. It seems necessary to secure additional analysis tools to provide complimentary fully-vectorial SE data analysis of nano-structured 2d and plasmonic materials. The finite difference time domain (FDTD) method presents attractive advantages as generality, ability to retrieve wide frequency range from single simulations as well as non-linear effects or non-periodic morphologies [4]. Previously, we have shown that the SE response of thin films can be obtained from FDTD using far-field projections of near-field simulation based on the FDTD method [5]. In this contribution we provide new results discussing the difficulties and strategies to needed to accurately model the SE response of non-periodic samples at large AoI. We will discuss the optimization of the modeling strategies and expected applications.

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References

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9:00am **C1-4 Analysis Procedures for Multiple Sets of Ellipsometric Spectra***, **Nikolas Podraza**, K Ghimire, P Uprety, M Junda,* University of Toledo, USA

Ellipsometric parameters are collected as a function of photon energy, spatial position on a sample, and time during a process. Analysis provides spectroscopic complex dielectric functions, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and structural information (layer thicknesses, surface roughness, interfaces). The particular photon energies measured can yield information pertaining to component layer intrinsic properties, with some regions of the spectrum more closely linked to particular material and electrical properties. Also, depending on material ε and the arrangement of materials in a sample, different spectral ranges are more or less sensitive to layer structure. To more fully understand the nature of materials comprising a sample, ellipsometric spectra are often measured over wide spectral ranges, using more than one instrument, and analyzed jointly. In other scenarios, multiple sets of ellipsometric spectra are collected either as functions of spatial position on a sample or time during a process to identify subtle material variations. Here we will discuss details of data analysis pertaining to four scenarios: (1) applying realistic parametric models of ε over the appropriate spectral ranges to deduce structural information, (2) simultaneous analysis of measurements collected from the millimeter (THz) to the ultraviolet spectral range using $\geq$2 ellipsometers, (3) utilizing spatially resolved mapping measurements to deduce material property variations, and (4) analysis of in situ time real time spectroscopic ellipsometry (RTSE) collected during thin film growth or post deposition modification. For (1) and (2) metal oxides will be considered, specifically aluminum doped zinc oxide (ZnO:Al) with particular attention to the analyzed spectral range dependence on resultant electrical properties. For (3), disordered nano-/polycrystalline semiconductors (Si:H, CdTe, $CuIn_{1-x}Ga_xSe_2$) for use in thin film solar cells will yield maps of thicknesses and degree of crystallinity. (4) Methylammonium lead iodide ($CH_3NH_3PbI_3$) perovskites will be monitored using RTSE during vapor deposition and post-deposition atmospheric exposure to track phase segregation into component CH_3NH_3I and PbI_2 as well as changes in the perovskite itself. The respective strengths and weaknesses of these methods are discussed.

9:20am **C1-5 High Precision Absorption Measurements in Optical Films using the TRACK Method: Comparison with the Laser-induced Deflection***, R Vernhes,* Polytechnique Montreal, Canada*; C Muhlig,* Leibniz-Institute of Photonic Technology (IPHT), Germany*; **Ludvik Martinu**,* Polytechnique Montreal, Canada

The accurate determination of optical constants of thin films is both challenging and critical for many optical applications. In this study, we focus on the methodology for the precise evaluation of the extinction coefficient (k) assessed by multi-angle spectrophotometry using the recently developed TRACK method [1]. More specifically, we present how absorption can be directly derived from transmission and reflection spectra in p polarization for complex samples showing non-idealities such as inhomogeneities, interfaces and thickness non-uniformity. As an example, we apply this method to a non-uniform inhomogeneous silicon nitride film deposited on glass and we demonstrate that the complete optical modeling of the non-idealities is not necessary to obtain k values. Finally, we compare the results determined by this method to those obtained by the highly sensitive laser induced deflection (LID) technique over a broad spectral range (400 to 1000 nm) and for various materials of interest for optical applications, such as TiO2, ZnO, silicon, etc.

1. R. Vernhes and L. Martinu, “TRACK – A new method for the evaluation of low-level extinction coefficient in optical films,” Optics Express 23 (2015) 28501.

9:40am **C1-6 Durability and Wear Mechanisms of Easy-to-clean Coatings on Glass and Displays Assessed by *in situ* Tribometry***, J Qian, T Schmitt, B Baloukas, **Jolanta Ewa Klemberg-Sapieha**, L Martinu,* Polytechnique Montreal, Canada*; C Kosik-Williams, J Price, E Null,* Corning Incorporated, USA

Fluorine-based easy-to-clean (ETC) coatings, with contact angles higher than 110º and friction coefficients of ~0.1, are widely applied on touch-screen displays to reduce staining and to enhance abrasion resistance.

In the present work, we evaluate the durability and study the wear mechanisms of ETC coatings on glass substrates using an *in situ* tribometer (TribTik) equipped with a camera system; this allows one to image, in real time, the contact area between the glass substrate and the abrading counterpart. Through this unique combination, the instantaneous friction coefficient and the contact area's status can be monitored and correlated *in situ,* thus offering the opportunity to abort the test at critical stages of the wear process and study its progression.

The morphology and composition of the wear tracks are further examined at different stages to understand the wear mechanisms of the ETC. We demonstrate, with the support of optical, SEM and EDX analyses that the instantaneous friction coefficient and the obtained *insitu* images correlate very well with the wear process. The progression of the wear mechanism is then defined as follows: 1) generation of unconsolidated debris, 2) formation of a layered tribofilm, 3) cracking of the tribofilm, and 4) damage to the underlying glass substrate.

10:00am **C1-7 Insitu Metrology for Surface Topography and Stress Characterization***, **Wojtek Walecki,*** Frontier Semiconductor, USA

Novel metrology tool for in-situ characterization of surfaces of coatings during deposition process. The tool measures the total integrated scatterer for smooth wafers when measuring forward, or back-reflection at very large angles of incidence. The tool is insensitive to vibrations and stray light. We discuss polarization resolved data and characterize our technique using NIST traceable standards. We discuss it's applications to semiconductor manufacturing.

The grazing angle reflection measurements were subject of radar [1], semiconductor [2], machine vision [3], space [4], traffic materials [5], and theoretical research [6]. The grazing angle forward reflection metrology was reported by us earlier [7], however, we are not aware of the fully polarization resolved grazing angle back-reflection metrology of roughness of functional coatings.

In addition we discuss recently developed polarization sensitive Raman scattering tool, and submicroradian and nanoradian beam deflection techniques for characterization of stress tensor in coatings on global and microscopic scale.

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10:20am **C1-8 Scratch Failure vs Residual Stress: a Relationship Applied to Optical Coatings***, T Poirié,* ***Thomas Schmitt,*** Polytechnique Montreal, Canada*; E Bousser,* University of Manchester, UK*; L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

The display industry became an engineering-driven sector which has shifted from mainly industrial uses to consumer products such as flat-panel displays, touch screens, multimedia devices, transportation, ophthalmic lenses and many others. The use of these devices implies various mechanical solicitations that become very critical in situations when sensitive substrates, such as polymers, are applied. Specifically, optical coatings in use today involve transparent ceramic-based materials which show a strong mechanical mismatch with the substrate. In addition, their typical thickness, which ranges from several tens to several hundreds of nanometers, makes their mechanical durability very challenging. It is therefore crucial to understand the failure mechanisms occurring during mechanical loading of these coated systems, and their relationships with the intrinsic properties such as internal stress.

In this work, we systematically study the scratch resistance and the delamination behavior of thin e-beam evaporated TiO_2 films deposited on plastic substrates. The use of Ion Beam Assisted Evaporation has been used to tailor the residual stress and to produce coatings which exhibit stress levels ranging from tensile to compressive. By combining an *in situ* scratch testing technique and a new approach based on reverse scratching sequence starting from high to low load, we were able to assess specific failure mechanisms in dependence on the stress level. Moreover, this method establishing the relationship between the scratch failure and the internal stress allows one to extract the yield strength, in the present context applied to model thin TiO_2 coatings. Finally, this study and the related methodology significantly enhances the understanding of the failure mechanisms occurring during scratch testing, and it can be applied to any optical and other films.

10:40am **C1-9 Fast Characterization of nm Thin to Thick Coatings using Pulsed-Rf Glow Discharge Optical Emission Spectrometry***, **Philippe Hunault**, M Chausseau, K Savadkouei,* HORIBA Scientific, USA*; P Chapon, S Gaiaschi,* HORIBA Scientific, France

Glow Discharge Optical Emission Spectrometry (GD-OES) provides direct measurement of the chemical composition of materials as a function of depth and can be used to characterize various coatings, made of both thin and thick layers, conductive or non-conductive materials

It consists in a pulsed radiofrequency glow discharge plasma source that is sputtering a large area of the material of interest and real time detection by a high resolution optical spectrometer of the sputtered species excited by the same plasma. All elements from H to U can be measured using this technique.

With its capability to perform depth profiling with a nanometric resolution and to go up to 150 µm deep into the sample within few minutes, GD-OES is an ideal tool to evaluate depth profiles on materials and to study interfaces between layers, diffusion processes or to optimize coatings processes. Many elements can be analyzed simultaneously, including Oxygen, Hydrogen, Deuterium, Carbon, Fluorine, Sulfur, Lithium… GD-OES is a versatile tool to study materials that complements other techniques such as XPS and SIMS.

Results obtained on various nm thin and thick oxide coatings, nitriding, carburizing, galvanization and energy storage will be shown. Examples of GD-OES as a tool for layer thickness determination will also be presented.

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