Spectroscopic Ellipsometry Focus Topic
Room 202A - Session EL+AS+EM-MoM

Application of SE for the Characterization of Thin Films and Nanostructures

Moderators: Alain C. Diebold, SUNY Polytechnic Institute, Mathias Schubert, University of Nebraska-Lincoln

8:20am **EL+AS+EM-MoM1 Stealth Technology-based Terahertz Frequency-domain Ellipsometry*, Vanya Darakchieva,*** Linköping University, Sweden **INVITED**

We present the newly designed Terahertz (THz) frequency-domain spectroscopy (FDS) ellipsometer at the Terahertz Material Analysis Center (THeMAC) at Linköping university and demonstrate its application to a variety of technologically important materials and heterostructures. We show that employing concepts used in stealth technology for the instrument geometry and scattering anti-static coating, and modulation of the backward wave oscillator (BWO) THz source allows for effective suppression of standing waves enabling accurate ellipsometry measurements with high spectral resolution (of the order of MHz). We further demonstrate an etalon-based method for frequency calibration in THz FDS ellipsometry. The instrument can incorporate various sample compartments, such as a superconducting magnet, in-situ gas cells or resonant sample cavities, for example. Reflection and transmission ellipsometry measurements over a wide range of angles of incidence for isotropic (Si) and anisotropic (sapphire) bulk samples are presented together with determination of the material dielectric constants. We further demonstrate results from cavity enhanced THz optical Hall effect experiments on an AlGaN/GaN high electron mobility transistor structure (HEMT), determining the free charge carrier density, mobility and effective mass parameters of the 2D electron gas (2DEG) at room temperature. We show through in-situ experiments on epitaxial monolayer graphene exposed to different gases and humidities that THz FDS ellipsometry is capable of determining free charge carrier properties and following their changes upon variation of ambient conditions in atomically thin layers. Exciting perspectives of applying THz FDS ellipsometry for exploring low-energy excitation phenomena in condensed and soft matter, such as the vibrational, charge and spin transport properties of magnetic nanolaminates, polymers and hybrid structures for photovoltaics and organic electronics; and determination of THz optical constants and signatures of security and metamaterials are envisioned.

9:00am **EL+AS+EM-MoM3 Spectroscopic Ellipsometry and Finite Element Modeling based Optical Characterization of Highly Coherent Au-Si Slanted Columnar Periodic Nanostructures*, Ufuk Kilic,*** University of Nebraska-Lincoln*; A. Mock,* Linköping University, Sweden*; R. Feder,* Fraunhofer IMWS, Germany*; D. Sekora, M. Hilfiker, R. Korlacki, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

An unprecedented and phenomenal control of anisotropic optical properties of a material is reported here by utilizing periodic arrangement of nanostructures. These artificially engineered structures exhibit distinct optical, mechanical, and magnetic properties when they are compared with their bulk counterparts which has recently gained a growing interest due to its potential applications in various optical and optoelectronic systems such as lenses, solar cells, photodetectors, and sensors [1-3]. In addition to the material choices (ie. elemental composition), the size and shape of these artificial structures also play a key role in tailoring the aforementioned inherent properties.

Unraveling the mechanisms that influence and control the optical properties of highly-porous, periodic, and three-dimensional arrangements of nanoplasmonic structures can offer new approaches for the development of next generation sensors. Glancing angle deposition and atomic layer deposition can be used to create periodic nanostructures with multiple constituent materials, so-called heterostructured metamaterials.[4] In this study, we employ a two-source (ie. Au and Si) electron-beam-evaporated, ultra-high-vacuum glancing angle deposition which allows for the fabrication of highly-ordered and spatially-coherent super-lattice type Au-Si slanted columnar heterostructured thin films. We perform a combinatorial spectroscopic generalized ellipsometry and finite-element method calculation analysis to determine anisotropic optical properties. We observe the occurrence of a strong locally enhanced dark quadrupole plasmonic resonance mode (bow-tie mode) in the vicinity of the gold junctions, with a tunable and geometry dependent frequency in the near-infrared spectral range. In addition, inter-band transition-like modes are observed in the visible to ultra-violet spectral regions. We demonstrate that changes in the index of refraction due to the concentration variation of a chemical substance environment (gaseous or liquid) within a porous nanoplasmonic structure can be detected by transmitted intensity alterations down to 1 ppm sensitivity.

References

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9:20am **EL+AS+EM-MoM4 Temperature Dependent Dielectric Function and Critical Point Comparison of bulk Ge and α-Sn on InSb*, Rigo Carrasco,*** *C. Emminger, N. Samarasingha, F. Abadizaman, S. Zollner,* New Mexico State University

Germanium is an indirect bandgap semiconductor with a bandgap of 1.55 µm at room temperature. Its band gap can be shifted to longer wavelengths and becomes direct by adding 5-20% Sn, which allows to detect efficiently in the IR range. Alloys of Ge and Sn are therefore of interest for photovoltaics, detectors and room temperature lasers (2-7 µm). Alpha-tin on the other hand, is a semimetal that, when under strain, has a very small band gap at the Gamma point of the Brillouin zone. We compare this direct band gap (E_0 peak) occurring in the infrared region of strained α-Sn on InSb to the absorption edge of Ge.

We investigate the temperature dependence of the complex dielectric function (DF) and interband critical points (CPs) of bulk Ge between 10 and 738 K using spectroscopic ellipsometry in the spectral range from 0.5 to 6.3 eV at a 70° angle of incidence [1]. The complex dielectric function at each temperature is fitted using a parametric oscillator model. Figure 1 shows that variations in temperature influence structures in the spectra of the DF. Furthermore, we analyze CPs in reciprocal space by studying Fourier coefficients as described in [2]. The peaks of the E_0 and $E_0+\Delta_0$ CPs are relatively narrow (Fig. 2) which makes the analysis of their broadenings difficult. A small excitonic peak is visible at the absorption edge E_0, also shown in Fig. 2.

Spectroscopic ellipsometry measurements were also performed on several epitaxially grown α-Sn layers on InSb in the spectral range of 0.03 to 6.5 eV. Comparing the results of the pseudo-dielectric function of Sn to the one of Ge shows a remarkable difference of both spectra in the IR- region, as demonstrated in Fig. 3. While structures at higher energies, such as the E_1 and $E_1+\Delta_1$ CPs, are similar in shape and amplitude for both materials, the E_0-peak in α-Sn is significantly larger than in Ge. Therefore, we believe that the E_0 peak in the spectrum of Sn is not due to excitons but can probably be explained by other parameters which influence the band structure, such as strain, composition, or free carrier concentration. The large peak between E_0 and E_1 is an interference fringe. We also compare the temperature dependence of the E_0 gap in Ge and alpha-tin.

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References

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9:40am **EL+AS+EM-MoM5 Elastomer Thin Films and Conducting Nanostructures for Soft Electronics and Dielectric Elastomer Transducers*, Bert Müller*,** *B. Osmani, T. Töpper,* University of Basel, Switzerland

Nanometer-thin polymer films are essential components of low-voltage dielectric elastomer transducers and will, for example, play a vital role in future artificial muscles [E. Fattorini et al.: Ann. Biomed. Eng. 44 (2016) 1355]. Organic molecular beam deposition (MBD) is a versatile technique to prepare silicone films under well-defined conditions [F. M. Weiss et al.: Mater. Design 105 (2016) 106; T. Töpper et al.: APL Mater. 4 (2016) 056101], but the achievable growth rates of about 1 µm per hour are too low for the fabrication of multi-layer devices. Therefore, we have developed electro-spraying as an alternative deposition method with one or two orders of magnitude faster rates [F. M. Weiss et al.: Adv. Electron. Mater. 2 (2016) 1500476; F. Weiss et al.: Langmuir 32 (2016) 3276]. For the two approaches, spectroscopic ellipsometry (SE) has been employed for in situ monitoring the film's optical properties, the film thickness and the surface morphology during deposition and ultra-violet (UV) light irradiation. The derived quantities were verified by means of atomic force microscopy (AFM). Subsequent to the silicone deposition and the cross-linking by UV light curing, Au has been deposited using MBD and sputtering. This deposition process was also quantitatively characterized using SE and controlled by means of the plasmonic fingerprints of the metal nanostructures [T. Töpper et al.: Adv. Electron. Mater. 3 (2017) 1700073]. The ex situ AFM measurements revealed well-known modulations characteristic for strained surface layers [B. Osmani et al.: Eur. J. Nanomed. 9 (2017) 69]. Recent nano-indentation tests have demonstrated that the Au-layers on the silicone near the critical stress regime hardly contribute to the overall elastic modulus and are, therefore, a sound basis for smart electrodes [B. Osmani et al.: Adv. Mater. Technol. 2 (2017) 1700105]. The nano-mechanical probing of the powered thin-film dielectric elastomer transducers evidenced the importance of the thickness homogeneity for such devices [B. Osmani et al.: Appl. Phys. Lett. 111, (2017) 093104]. The function of planar thin-film dielectric elastomer transducers can be precisely determined taking advantage of the cantilever bending approach [B. Osmani et al.: Rev. Sci. Instrum. 87 (2016) 053901]. Spectroscopic ellipsometry and advanced atomic force microscopy with nano-indentation capability enables us to thoroughly characterize the film morphology as well as the optical and local mechanical parameters of silicone and Au/silicone nanostructures.

10:00am **EL+AS+EM-MoM6 Spectroscopic Ellipsometry Investigation of Temperature Effects in Heated Self-organized 2D Arrays of Au Nanoparticles***, **Michele Magnozzi**, M. Ferrera, M. Canepa,* Università di Genova, Italy*; F. Bisio,* CNR-SPIN, Italy

Metal nanoparticles (NPs) have the interesting property of behaving as efficient converters of EM radiation into heat. While this can occur via interband photoexcitation, the presence of a Localized Surface Plasmon Resonance provides an extra degree of freedom to tune and optimize the heating [1].

Assessing the temperature of plasmonic NPs during or immediately after illumination is not an easy task, and typically involves the use of models that necessarily have to simplify the complex temperature-dependent dielectric and thermodynamic response of nanosystems; for this reason, a measurement of the T-dependent optical behavior of the NPs at well-defined, externally controlled T would greatly contribute towards a better understanding of the thermoplasmonic properties of metal NPs.

Spectroscopic ellipsometry (SE), being a high-sensitive and non-destructive technique, is an ideal tool to investigate the optical response of NPs systems, provided that a proper model is used for data analysis.

We report a T-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [2]. SE measurements were acquired in the 245-1450 nm spectral range, under high-vacuum conditions and in the 25-350 °C temperature interval [3]. Using a dedicated effective medium approximation developed for this kind of systems [2], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by *ex-post* AFM analysis; the temperature-dependent dielectric functions of Au, required as input in the model, was obtained in a dedicated SE measurement. The model yields a very good agreement with experimental data at relatively low T; however, though the appropriate T-dependent dielectric function of Au is systematically employed, the model is no longer able to reproduce the data obtained at the highest T. Indeed, a satisfactory agreement is attained introducing an effective correction to the Drude term of the dielectric function of Au, that keeps into account morphological effects affecting the NPs surface - such as softening or melting - that enhance the surface electron scattering rate. Our analysis thus shows that the T-dependent optical properties of metal NPs deviate from simplified expectations, and validate SE as valuable tool to study the complex, anisotropic properties of plasmonic NPs systems.

References

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10:40am **EL+AS+EM-MoM8 Spectroscopic Ellipsometry of 2D WSe_2 Films***, **Baokun Song**, H.G. Gu, M.S. Fang,* Huazhong University of Science & Technology, China*; Y.L. Hong, W.C. Ren,* Shenyang National Laboratory for Materials Science Institute of Metal Research Chinese Academy of Sciences, China*; X.G. Chen, S.Y. Liu,* Huazhong University of Science & Technology, China

Recently, two-dimensional (2D) WSe_2 has become a popular choice for nanoelectronic, optoelectronic, and valleytronic devices due to its layer-modulated bandgap, high mobility (~$200cm^2V^{-1}s^{-1}$) and on-off ratio (10^8), and large spin-orbit coupling effect. The performance of those novel WSe_2-based devices strongly depends on the intrinsic optical properties of WSe_2, which exhibit an intriguing layer dependency. Therefore, the accurate and quantitative characterization of the layer-dependent optical properties of WSe_2 is essential to the optimal design of those related devices.

In this work, the dielectric function, bandgaps, and critical points (CPs) of WSe_2 ranging from monolayer to bulk have been comprehensively investigated and analyzed by spectroscopic ellipsometry over an ultra-broad band (0.73-6.42eV). The dielectric function of high-quality uniform WSe_2 specimens prepared by chemical vapor deposition were firstly obtained from the ellipsometric spectra. Then the bandgaps of the WSe_2 films were determined from their corresponding absorption coefficient spectra. We experimentally observed that the bandgaps of the WSe_{-2} films change from 1.63eV in monolayer to 1.21eV in bulk. Moreover, by using the CPs analysis, a series CPs (A-H) in the dielectric function spectra were precisely distinguished and many of them were rarely reported before. The positions of CPs (A-E) exhibit an obvious red shift when the layer number increases, while the CPs (F-H) exhibit a slight blue shift. The former phenomenon can be partly interpreted as the decaying geometrical confinement of excitons, while the underlying reasons for the latter merit further studies. These novel and advanced optical features will promote the fundamental understanding of the electronic structures and the development of WSe_2-based devices.

11:00am **EL+AS+EM-MoM9 Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry***, X.Q. Wang, X.Y. Shan, H. Siddique, **Rucheng Dai**, Z.P. Wang, Z.J. Ding, Z.M. Zhang,* University of Science and Technology of China

Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry

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Abstract

During the last few years, the hybrid organic-inorganic methylammonium lead halide perovskite $CH_3NH_3PbI_3$ ($MaPbI_3$) has received great interest in the field of photovoltaics [1,2]. The relevant researches develop rapidly since the first realization of organic-inorganic hybrid solar cell, due to the excellent performance of $MaPbI_3$, such as high charge mobilities, suitable band gap and long carrier diffusion length. However the stability of MaPbI has been a key issue hinder the practical application [3]. Here we present in-situ spectroscopic ellipsomety measurement to understand the nature of thermal degradation process of MaPbI . The dynamic evolution process of dielectric constants of the as-prepared $MaPbI_3$ film through heating is obtained by an effective medium approximation model fitting. The proportion of $MaPbI_3$ and PbI is also obtained from the analysis of the ellipsometry data. The thickness of the film decrease in two-step, which is explained as the collapse of the PbI_2 frame. Our work provide the first in-situ detection of the optical properties through the degradation process of $MaPbI_3$ film, which can be consulted for further improving the stability of $MaPbI_3$.

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11:20am **EL+AS+EM-MoM10 a-Si as a Protective Layer to Block the Oxidization of Al mirrors**, ***Yhoshua Wug***, University of California at Los Angeles; *D.D. Allred, R.S. Turley,* Brigham Young University

Arguably, the best path to produce a truly broadband, e.g., an IR-optical-UV-EUV (extreme ultraviolet) mirror, for a future space observatory is an EUV multilayer mirror coated by a very thin bare aluminum layer. However, using a bare Al layer presents challenges that first must be overcome. Al oxidizes rapidly when contact with the atmosphere occurs. The customary solution is to cover the mirror with a protective evaporated fluoride layer. Unfortunately, these are opaque under ~110 nm, whereas, bare Al itself is highly reflective down to 85nm and could be used as a mirror to that wavelength if a barrier were not required. Once the mirror is in space far from the Earth, where there is no oxygen, Al would no longer need a barrier layer. Could a barrier be removed in space? Neither fluorides nor aluminum oxide can be removed once they are deposited without damaging the mirror's surface and destroying VUV reflectance. a-Si could be used as a protective layer that is potentially removable without roughening the Al surface. Dry hydrogen etching processes exist that could remove a silicon barrier as silane gas which would dissipate quickly in space. Such a process would use the Al layer as an etch stopping barrier in removing the a-Si protective layer. But is a-Si a suitable barrier for Al? We report our variable-angle spectroscopic ellipsometry studies of evaporated a-Si thin films on evaporated Al films. We discuss the conditions where a-Si can act as a protective layer to block aluminum oxidation.

11:40am **EL+AS+EM-MoM11 Terahertz to Mid-infrared Dielectric Response of Poly-methacrylates for Stereolithographic Single Layer Assembly**, *D.B. Fullager,* ***Serang Park****, Y. Li, J. Reese,* University of North Carolina at Charlotte; *E. Sharma, S. Lee,* Harris Corporation; *S. Schöche, C.M. Herzinger,* J.A. Woollam Co. Inc; *G.D. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Producing THz optical components with arbitrary shapes using additive manufacturing is receiving considerable interest because it offers a rapid, low-cost avenue for THz imaging system development. In order to design such THz optical components appropriately, accurate knowledge of the complex dielectric function of the materials used for stereolithographic 3D fabrication, is crucial. In this presentation we report on the complex dielectric function of several poly-methacrylates which are frequently used for stereolithographic fabrication. Spectroscopic ellipsometry data sets from the THz to mid-infrared spectral range were obtained from isotropically cross-linked poly-methacrylate samples. The data sets were analyzed using stratified layer optical model calculations using parameterized model dielectric functions. While the infrared spectral range is dominated by several strong absorption features with Gaussian profiles, these materials are found to exhibit only weak absorption in the THz range. In conclusion we find that thin transmissive THz optics can be easily achieved using poly-methacrylate-based stereolithographic fabrication. Possible origins of the observed absorption in the THz spectral range are identified and pathways to reduce it are discussed.

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