## Spectroscopic Ellipsometry Focus Topic
## Room 9 - Session EL+AS+EM+TF-MoM

### Application of SE for the Characterization of Thin Films and Nanostructures

**Moderator:** Tino Hofmann, University of North Carolina at Charlotte

8:20am **EL+AS+EM+TF-MoM-1 Ultra-thin Plasmonic Metal Nitrides: Optical Properties and Applications**, ***Alexandra Boltasseva,*** Purdue University **INVITED**

Transition metal nitrides (e.g. TiN, ZrN) have emerged as promising plasmonic materials due to their refractory properties and good metallic properties in the visible and near infrared regions. Due to their high melting point, they may be suitable for high temperature nanophotonic applications. We have performed comprehensive studies of the temperature induced deviations to the dielectric function in TiN thin films. The studies were conducted on 30 nm, 50 nm, and 200 nm TiN films on sapphire substrates at temperatures up to 900 0C in the wavelength range 350-2000 nm using a custom built in-situ high temperature ellipsometry setup. The results were fitted with a Drude-Lorentz model consisting of one Drude oscillator and 2 Lorentz oscillators. As the temperature is elevated, the real and imaginary parts both begin to degrade. However, the deviations to the optical properties of TiN are significantly smaller compared to its noble metal counterparts, with no structural degradation in the TiN films. In addition to high temperature applications, TiN could also be a potential material platform for investigating light-matter interactions at the nanoscale, since high quality, continuous films of TiN can be grown on substrates such as MgO and c-sapphire down to just a few monolayers. Ultrathin TiN films with thicknesses of 2, 4, 6, 8, and 10 nm were grown on MgOusing DC reactive magnetron sputtering, resulting in high quality films with low roughness. The changes in the linear optical properties were investigated using variable angle spectroscopic ellipsometry at angles of 50° and 70° for wavelengths from 400 nm to 2000 nm. A Drude-Lorentz model consisting of one Drude oscillator and one Lorentz oscillator was used to fit the measurements. As the thickness decreased, an increase in the losses and a decrease in the plasma frequency was observed. However, the films remained highly metallic even at 2nm, demonstrating that they could be used for nanophotonicapplications, including nonlinear optical devices and actively tunable plasmonic devices.

9:00am **EL+AS+EM+TF-MoM-3 Magnetron Sputtering of TiN Coatings: Optical Monitoring of the Growth Process by Means of Spectroscopic Ellipsometry*****, Jiri Bulir,*** *J More Chevalier, L Fekete, J Remiasova, M Vondracek, M Novotny, J Lancok,* Institute of Physics ASCR, Czech Republic

The plasmonic applications requires search for novel materials with metal-like optical properties and low optical losses. Transition metal nitrides such as TiN, TaN, ZrN, HfN, NbN exhibit metallic properties depending on concentration of free-carrier of charge. Their plasmonic properties can be tuned by deposition parameters controlling the film structure and the stechiometry.

In this work, we deal with study of growth process of TiN films. The films are grown by RF magnetron sputtering on fused silica, silicon and MgO substrates at substrate temperature ranging from 20°C to 600°C. The growth process is monitored using in-situ spectral ellipsometer in spectral range from 245 to 1690 nm. The ellipsometric data, which are obtained during the deposition process, are attentively analysed using mathematical models based on Drude-Lorentz oscillators.

The Lorentz oscillators are used for description of interband transition in ultraviolet and visible spectral range, whereas the Drude oscillator describes the free-electron behavior in the infrared spectral range. We show that the free-electron behavior is affected by thickness of the ultrathin coatings due to electron scattering effects at the interfaces. Number of physical parameters such as free-electron concentration, Drude relaxation time and electrical conductivity is estimated at each stage of the deposition process by analysis of dielectric functions using the mentioned model. The resulting evolution of the electrotransport properties during the TiN film growth is presented. Special attention is devoted to the initial nucleation stage when the free-electron behaviour is significantly influenced by the interface between the substrate and the TiN film. Based on evolution of electrotransport properties, we discuss differences between polycrystalline growth of TiN film on Si and fused silica substrates and epitaxial growth on MgO substrates.

The accomplished TiN coatings are analyzed using infrared ellipsometer operating in spectral range from 1.7µm to 30µm where the optical constants are infuenced most importantly by free-electron behaviour. The obtained results are compared with those obtained by the in-situ ellipsometer. Special attention is focused on scattering of free electrons at grain boundaries and at the TiN layer interfaces. The estimated parameters are correlated with structure changes such as grain coarsening and surface morphology. The crystallinity is analysed by X-ray Difractometry. The surface morphology of the completed coatings is studied using Atomic Force Microscopy and Scanning Electron Microscopy. The TiN film stechiometry is estimated by X-ray Photoemission Spectroscopy.

9:20am **EL+AS+EM+TF-MoM-4 Variable Temperatures Spectroscopic Ellipsometry Study of the Optical Properties of InAlN/GaN Grown on Sapphire**, *Y Liang,* Guangxi University, China*; H Gu,* Huazhong University of Science and Technology, China*; J Xue,* Xidian University, China*;* ***Chuanwei Zhang***, Huazhong University of Science and Technology, China*; Q Li,* Guangxi University, China*; Y Hao,* Xidian University, China*; S Liu,* Huazhong University of Science and Technology, China*; Q Yang, L Wan, Z Feng,* Guangxi University, China

Indium aluminum nitride (InAlN), a prospective material for lattice matched confinement layer, possesses the potential to improve the reliability and performance of high electron mobility transistors (HEMTs).[1] One of the important advantages of InAlN alloy is the possibility of growing in-plane lattice-matched to GaN for an indium content of around 17%. However, the bandgap we expected is hindered by the growth of high-quality InAlN films due to the phase separation and nonuniform composition distribution.[1-2]

In this work, InAlN/GaN heterostructures, grown by pulsed metal organic chemical vapor deposition (PMOCVD) on c-plane sapphire substrates, were investigated by a dual rotating-compensator Mueller matrix ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co. Ltd., China). The experimental data (Ψ and Δ), covering the wavelength (λ) range from 193 nm up to 1700 nm at 1 nm step or energy (E) from 0.73 eV to 6.43 eV, were obtained by variable temperatures spectroscopic ellipsometric (VTSE) in three angles (50°, 55° and 60°). The Eoptics software was utilized to fit VTSE data using Tauc-Lorentz multiple oscillator modes. By analyzing the fitting results, the optical constants of the InAlN at variable temperatures (25℃-600℃) were obtained. The peak value of the refractive index increases from 269 nm to 284 nm with increasing temperature. The bandgaps are 4.57 eV and 4.35 eV at the temperature 25℃and 600℃, respectively. These results demonstrated that InAlN/GaN has a high thermal stability, scilicet no significant performance degradation in high temperature environment.

Reference

[1] Wenyuan Jiao, Wei Kong, Jincheng Li et al, Characterization of MBE-grown InAlN/GaN heterostructures valence band offsets with varying In composition, AIP ADVANCES 6, 035211 (2016).

[2] JunShuai Xue, JinCheng Zhang, Yue Hao, Investigation of TMIn pulse duration effect on the properties of InAlN/GaN heterostructures grown on sapphire by pulsed metal organic chemical vapor deposition, Journal of Crystal Growth 401, 661 (2014).

9:40am **EL+AS+EM+TF-MoM-5 Optical Properties of Cs$_2$AgIn$_{(1-x)}$Bi$_x$Cl$_6$ Double Perovskite Studied by Spectroscopic Ellipsometry*****, Honggang Gu,*** *S Li, B Song, J Tang, S Liu,* Huazhong University of Science and Technology, China

During the past several years, the organic-inorganic lead halide perovskites (APbX$_3$, A = CH$_3$NH$_3$ or NH$_2$CHNH$_2$, X = Cl, Br, or I) have been promising materials for photovoltaic, photoelectric -detecting and light-emitting devices due to their outstanding photoelectric properties, such as broad absorption range, high quantum efficiency, ultrafast charge generation, high charge carrier mobility and long charge carrier lifetime and diffusion length. However, there are two remaining challenges that need to be addressed in order to apply these materials to photoelectric productions, namely the compound stability and the presence of lead. Most recently, lead-free metal halide double perovskites, such as Cs$_2$AgBiCl$_6$ and Cs$_2$AgInCl$_6$, have attracted extensive attention because of their nontoxicity and relative air-stability. In the study and application of these perovskite materials, the knowledge of their optical properties, such as the bandgap and the basic optical constants, is of great importance to predict the photoelectric characteristics and dig the potential of the materials.

Spectroscopic ellipsometry (SE) has been developed as a powerful tool to characterize the optical properties as well as structure parameters of novel materials, thin films and nanostructures. In this work, we study the optical properties of Cs$_2$AgIn$_{(1-x)}$Bi$_x$Cl$_6$ perovskites by a spectroscopic ellipsometer

(ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China). The refractive index and the extinction coefficient of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ with different composition coefficient *x* of bismuth are determined by the ellipsometer over the wavelength range of 250-1000nm. We find that the presence of bismuth introduces two critical points in the optical constant spectra of the perovskites, i.e., 315nm and 382nm in the refractive index spectra and 300nm and 375nm in the extinction coefficient spectra, respectively. Moreover, there is a red shift in the bandgaps and significant increase in both the refractive index and the extinction coefficient with the increase of composition coefficient *x* of bismuth.

10:00am **EL+AS+EM+TF-MoM-6 Charge Carrier Dynamics of Aluminum-doped Zinc Oxide Deposited by Spatial Atomic Layer Deposition***, **Daniel Fullager**, G Boreman, T Hofmann,* University of North Carolina at Charlotte*; C Ellinger,* Eastman Kodak Company

Transparent conductors for displays, backplanes, touchscreens and other electronic devices are an area of active research and development; in this manner, aluminum-doped zinc oxide (AZO) has shown promise as an ITO replacement for some applications. Although there have been numerous reports on the optical properties and electrical conductivity of AZO, there has not yet been a Kramers-Kronig consistent dispersion model fully describing the charge carrier dynamics. In this presentation, we will report on the model dielectric function of AZO from the combination of UV-Vis and IR spectroscopic ellipsometry. A model dielectric function that describes the optical response over this wide spectral range will be presented and discussed. In particular, we will present a comparison between the commonly used extended Drude models and the dielectric function developed here in light of results obtained from density functional theory calculations.

The AZO films analyzed in this study were deposited using a spatial atomic layer deposition (SALD) process. While AZO can be deposited by several techniques, including sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD), ALD does allow for the greatest ability to control the aluminum-doping level of AZO. However, the range of substrate sizes and form factors addressable by traditional chamber ALD are limited. Conversely, spatial ALD (SALD) is an atmospheric pressure, roll-compatible ALD process that enables the materials property control of ALD to be translated into a wider range of applications spaces. Furthermore, the use of selective area deposition in a “patterned-by-printing” approach enables the high-quality AZO deposited by SALD to be easily patterned, offering an integrated and facile path for manufacturing optical and electronic devices.

10:40am **EL+AS+EM+TF-MoM-8 Broad Range Ellipsometry Shining Light onto Multiphase Plasmonic Nanoparticles Synthesis, Properties and Functionality***, **Maria Losurdo**,* CNR-NANOTEC, Italy **INVITED**

How rich are the physics, interface chemistry and optical properties associated with the surface plasmons of metal nanostructures and their potential for manipulating light at the nanoscale! For many technological applications nanoparticles (NPs) are supported on a substrate, and at the nanoscale, interaction and interfaces with the support become very important. We have demonstrated that the substrate/NPs interaction is the key to engineering not only the shape but also the crystalline phase of NPs.

This contribution will present and explore fundamental and applied aspects of multiphase core-shell plasmonic NPs supported on substrates of technological interest using various diagnostic tools, which comprise: (i) spectroscopic ellipsometry spanning the THz, IR, visible, and UV wavelength ranges, (ii) variable angle Muller Matrix ellipsometry to qualify size effects on anisotropy and depolarization of samples, (iii) *in-situreal-time* spectroscopic ellipsometry to understand growth and tailor particle size which ultimately controls the plasmon resonance, and (iv) various imaging and microscopies techniques to elucidate the interplay between the nanostructure of multiphase nanoparticle and their functionality.

The case studies involve liquid-shell/solid-core plasmonic NPs (Ga, Ga/Mg), plasmon-catalytic core/shell Ga/Pd and plasmon-magnetic Ni/Ga NPs supported on various substrates (glass, plastics, sapphire) that control their crystalline phases.

We will start with a description of the *real-time* ellipsometry capabilities in monitoring the growth of those multiphase core/shell NPs to detect the formation of the various phases in situ and to control the resulting plasmon resonance.

The discussion then will shifts to a description of fundamental of thermodynamics of substrate supported multiphase NPs and how their growth dynamics is controlled by the interface energies, and how those new phenomena can be highlighted by real-time ellipsometry.

Ex-situ corroborating measurements of Mueller-matrix ellipsometry and hyperspectral cathodoluminescence spectroscopy and imaging will be presented to discuss phenomena of depolarization and of interaction of NPs resulting from the self-assembly.

Finally, since those NPs enable active plasmonics, we demonstrate the implications of the multi-phase nature of NPs, as well as solid-liquid phase coexistence on the plasmon resonance (LSPR) of supported NPs and on its exploitation to follow in real time phenomena in their application in catalysis (hydrogen storage and sensing) and optomagnetism and possible future directions.

*The contribution of the H2020 European programme under the project TWINFUSYON (GA692034) is acknowledged*

11:20am **EL+AS+EM+TF-MoM-10 Use of Evolutionary Algorithms for Ellipsometry Model Development and Validation using Eureqa***, **Neil Murphy**,* Air Force Research Laboratory*; L Sun,* General Dynamics Information Technology*; J Jones,* Air Force Research Laboratory*; J Grant,* Azimuth Corporation

Eureqa, developed by Nutonian Inc., is a proprietary modeling engine based on automated evolutionary algorithms. In this study, we utilized Eureqa to parameterize both the amplitude and phase difference data for reactively sputtered thin films. Specifically, evolutionary algorithms are used to develop and validate models for fitting raw ellipsometric data for a variety of optical materials including $SiO_2$, Ta-$_2$O$_5$, and Aluminum Zinc Oxide. These films, deposited using pulsed DC magnetron sputtering, were deposited on both silicon and fused quartz substrates, and measured using a J.A. Woollam VASE system. The resulting models are then compared to traditional models that are currently utilized to fit the candidate materials systems.

11:40am **EL+AS+EM+TF-MoM-11 Excitonic Effects on the Optical Properties of Thin ZnO Films on Different Substrates***, **Nuwanjula Samarasingha**, Z Yoder, S Zollner,* New Mexico State University*; D Pal, A Mathur, A Singh, R Singh, S Chattopadhyay,* Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the $E_1$ critical points are strongly enhanced by two-dimensional excitons. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. In addition to these semiconductors, wide band gap materials like ZnO exhibit strong excitonic features in the dielectric function (ε) which is directly related to the electronic band structure. The top valence band at the Γ point in the Brillouin zone is split into three bands by spin orbit and crystal field splitting. The corresponding free exciton transitions between the lowest conduction band and these three valence bands are denoted by A, C ($\Gamma_7$ symmetry) and B ($\Gamma_9$ symmetry). The transition from the B subband is forbidden for light polarized parallel to the optical axis (extraordinary dielectric function). ZnO is attractive for optoelectronic device applications due to its large excitonic binding energy of 60 meV at room temperature.The influence of this excitonic absorption on ε was described by Tanguy [1].

Here we investigate the behavior of excitons in c-oriented ZnO thin films grown on Si (smaller band gap than ZnO) and $SiO_2$ (larger band gap than ZnO) substrates using variable angle spectroscopic ellipsometry and FTIR ellipsometry. We also performed X-ray diffraction (XRD), X-ray reflectivity (XRR), and atomic force microscopy (AFM) to characterize the structural properties of our ZnO films.

In a thin epitaxial layer on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In ZnO (band gap 3.37 eV) grown on a large-gap $SiO_2$ substrate (type-I quantum well), both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin ZnO layers on $SiO_2$ are much larger than in the bulk and increase monotonically with decreasing thickness.

On the other hand, in a staggered type-II quantum well (ZnO on Si), either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element is strongly reduced. Therefore, ε of thin ZnO layers on Si is much smaller than in the bulk and decreases monotonically with decreasing thickness. We will fit our ellipsometric spectra by describing the dielectric function of ZnO using the Tanguy model [1]. We will analyze the dependence of the excitonic Tanguy parameters on quantum well thickness and substrate material.

Reference:

[1] C. Tanguy, Phys. Rev. Lett. **75**, 4090 (1995).

# Author Index

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