Fundamentals and Technology of Multifunctional Materials and Devices
Room Sunrise - Session C1

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

Moderators: Nikolas Podraza, University of Toledo, Juan Antonio Zapien, City University of Hong Kong

1:50pm **C1-2 Design Principles for Binary and Multicomponent Conductive Nitrides for Applications in Electronics Plasmonics and Photonics*, Panos Patsalas,*** Aristotle University of Thessaloniki, Greece*; N Kalfagiannis,* Nottingham Trent University, UK*; S Kassavetis,* Aristotle University of Thessaloniki, Greece*; G Abadias,* Université de Poitiers, France

Although conductive nitrides, such as TiN, ZrN, and $Ti_xAl_{1-x}N$, were intensively studied for mechanical applications since 1980s and as diffusion barriers since 1990s, their combination of thermal and mechanical stability, with the compatibility of their growth to CMOS fabrication, and with their refractive character and electronic conductivity, paved the way for their emergence as important plasmonic and photonic materials [Naik, G.V. *et al*, Adv. Mater. 25 (2013) 3264-3294; Kassavetis, S. *et al*, Surf. Coat. Technol. 295 (2015) 125-129; Kassavetis *et al*, Appl. Phys. Lett. 108 (2016) art. No. 263110; Metaxa *et al*, ACS Appl. Mater. Inter. 9 (2017) 10825-10834]. In this work, we review the optical properties, in terms of ellipsometry, FTIR spectroscopy, and XPS valence band spectra, of a wide range of binary (TiN, ZrN, HfN, VN, NbN, TaN, MoN, WN) and multicomponent ($Ti_xMg_{1-x}N$, $Ti_xSc_{1-x}N$, $Ti_xAl_{1-x}N$, $Ti_xZr_{1-x}N$, $Ti_xHf_{1-x}N$, $Ti_xNb_{1-x}N$, $Ti_xTa_{1-x}N$, $Ti_xMo_{1-x}N$, $Ta_xZr_{1-x}N$) films and we establish correlations between their optical behavior, electron conductivity and work function with the intrinsic (*e.g.* the valence electron configuration of the constituent metal) and extrinsic (*e.g.* point defects and microstructure) factors. We also correlate the plasmonic performance of nitride nanostructures and nitride/dielectric interfaces with the electron density of states of their valence band. We demonstrate that, indeed TiN and ZrN along with HfN are the most well-performing plasmonic materials in the visible range, while VN and NbN may be viable alternatives for plasmonic devices in the blue, violet and near UV ranges, albeit in expense of increased electronic loss. WN is disregarded as candidates for plasmonics, opposing recent theoretical works, due to the excessive concentration of point defects, even in epitaxial form. Finally, TaN has a substantial plasmonic activity in the metastable, cubic rocksalt structure, however, in most cases tends to form mixed cubic-hexagonal samples that are also excessively lossy. Furthermore, we consider the alloyed ternary conductive nitrdes and by critical evaluation and comparison, we identify the emerging optimal tunable plasmonic conductors among the immense number of alloying combinations. As a result, we provide design principles of nitride conductors for plasmonic, photonic, and optoelectronic devices, such a nanoantennas, SERS-based biosensors, selective absorbers of solar or other radiation, stable Bragg-mirrors, epsilon-near-zero (ENZ) metamaterials, and ohmic contacts for light emitting diodes based on III-V semiconductors.

2:10pm **C1-3 Tip Enhanced Optical Microscopy and Spectroscopy Based on Near Field Force Detection – a Review*, H. Kumar Wickramasinghe,*** University of California, Irvine, USA **INVITED**

Near field scanning optical microscopy (NSOM) has evolved into a rich field of study with many different variants over the past 25 years. Many different modes of NSOM based on apertureless/scattering NSOM techniques have evolved such as near-field fluorescence and Tip Enhanced Raman Spectrosocopy (TERS) etc. All these techniques are based on measuring a local tip enhanced near-field interaction in the far field. In this talk we present a review of a new modality where optical microscopy/spectroscopy is performed by measuring the dipole-dipole interaction force between an optically driven sample and a dipole created in the tip – here, a near field optical interaction is measured *in the near-field*. Photo induced force microscopy (PIFM) is capable of measuring both the linear and non-linear optical response of a sample on the nanoscale. We will present recent experimental and theoretical data both in the visible and in the mid infra-red.

2:50pm **C1-5 Crystallite Grain Orientation Manipulation through Deposition Flux Angle and Composition in $CdSe_{1-x}Te_x$*, Dipendra Adhikari,*** *M Junda, C Grice, P Koirala, Y Yan, R Collins, N Podraza,* University of Toledo, USA

Cadmium telluride (CdTe) based semiconductors are of interest as absorber layers for thin film photovoltaics. In particular, alloying with selenium ($CdSe_{1-x}Te_x$) has helped to significantly improve device efficiency by reducing parasitic absorption losses in the vicinity of the n-type heterojunction partner. Here microstructural properties of two series of films are studied using grazing incidence x-ray diffraction measurements (GIXRD), scanning electron microscopy, and spectroscopic ellipsometry. A CdTe series consists of films deposited by sputtering onto soda lime glass substrates mounted at 0°, 45°, 55°, 65°, 75°, and 85° source flux angles relative to the substrate normal (i.e. glancing angle deposition). A $CdSe_{1-x}Te_x$ series is fabricated by co-sputtering CdSe and CdTe with varying combinations of individual cathode powers resulting in a film series that spans the full range of compositions from x = 0 to 1. Influence of deposition angle and film composition on resultant crystalline grain size and orientation are tracked for these films. All CdTe films studied are found to have cubic crystal structure and (111) preferential grain orientation. Films deposited at 0° and 45° are almost entirely (111) oriented, whereas films deposited at intermediate angles exhibit a wider variety of competing grain orientations, suggesting that deposition angle can be used as an effective parameter towards controlling grain orientation. With increasing numbers of grain orientations, grain size is found to decrease. $CdSe_{1-x}Te_x$ alloys exhibit diffraction peaks corresponding to both cubic and hexagonal crystal systems. The films have a (111) preferred grain orientation that shifts from lower to higher values of 2ϑ with increasing Se content. These $CdSe_{1-x}Te_x$ films are measured in both as-deposited and $CdCl_2$ treated states with all $CdCl_2$-treated samples having increased grain size compared to corresponding as-deposited samples. Generally, the diffraction patterns transition from CdSe-like to CdTe-like with increasing x. However, interesting behavior is observed for intermediate compositions, such as the (103) diffraction peak corresponding to hexagonal crystal system becoming relatively strong for a few compositions with low x, but being weak for all others.

3:10pm **C1-6 Durable Electrochromic Coating Systems for Advanced Smart Windows and Security Devices***, F Blanchard, B Baloukas, S Loquai, J Klemberg-Sapieha,* ***Ludvik Martinu,*** Polytechnique Montréal, Canada

The present work is our latest contribution to the development of large area smart windows based on electrochromic materials that have yet to properly breach the market due to the following main limitations: 1) the fabrication costs are still quite high, and 2) the durability of the system as a whole still requires significant improvements.

In response, this study offers a highly attractive and counterintuitive solution to both of these issues. Traditional WO_3 films, the main constituent of electrochromic windows, are traditionally deposited by magnetron sputtering at relatively high pressures (10-30 mTorr) to generate sufficient porosity and thus ensure a high ionic mobility. In this work, we explore a new and different approach to control the porosity involving intense ion bombardment during deposition at low pressures (< 5 mTorr). The resulting films' performance is tested through cyclic voltammetry using both H+ and Li+ ions and other complementary methods. We systematically categorize the coating properties based on their coloration efficiency, dynamic behavior and chemical durability. The present ion bombardment approach leads to a deposition rate increase of five times compared to the standard fabrication method, while the long term stability is significantly enhanced. The film characteristics are explained in terms of a microstructural model based on the formation of a unique nanocrystalline porous structure. In combination with an appropriate control of the surface reactions, this offers a possibility to tailor the transmission and reflection spectra of such coatings with enhanced durability for various applications such as advanced glazings for architectural glass, color shifting active security and authentication devices, and others.

3:30pm **C1-7 From "n" and "k" to Solar Cell Functionality: The Importance of Optical Property Characterization*, Nikolas Podraza,*** *M Junda, I Subedi, K Ghimire,* University of Toledo, USA

Predominate types of photovoltaic (PV) technologies studied at present were invented in the last century. Industrially manufactured devices based on wafer silicon (Si) and thin film cadmium telluride (CdTe) still have relevant problems with respect to their characterization. Methylammonium lead iodide perovskite (CH3NH3PbI3) materials have recently achieved very high efficiency when implemented as PV absorber layers. Here the optical properties of layers in each of these types of devices will be discussed. For "past-to-present" generation materials, Si wafer based PV with aluminum (Al) back surface fields (BSF) are modeled with particular attention paid to the characterization of Al+Si interfacial region optical properties as obtained by through-the-Si spectroscopic ellipsometry. When Al+Si optical properties are obtained and incorporated into the ray-tracing simulation of Si wafer solar cell modules, good convergence is obtained between those simulations and experimental results also with device performance parameters such as short circuit current density (Jsc) from quantum efficiency simulations (QE) aligned with experimental results. Next, "present" generation thin film PV including CdTe device structures are characterized by through-the-glass spectroscopic ellipsometry and modeled with QE based on reference optical properties to illuminate sources of optical and electrical losses. When CdTe is alloyed with selenium (Se), the band gap is narrowed and device performance is altered both in simulation in experimental QE results. Similarly, "future" generation CH3NH3PbI3 perovskite based solar cells are characterized by through-the-glass ellipsometry with QE modeling matching experiment. Band gap narrowing of this class of perovskites is characterized with spectroscopic ellipsometry. The resulting optical constants are used in the simulation of perovskite based single junction and tandem junction solar cells.

3:50pm **C1-8 Bipolar Resistive Switching Performance of MoS_2 Based ReRAM Devices using WN as Bottom Electrode for Non-volatile Memory Application***, **Ravi Prakash**, S Sharma, D Kaur,* Indian Institute of Technology Roorkee, India

The reproducible resistive switching characteristics of sputtered deposited MoS_2 thin film has been investigated in Cu/MoS_2/WN stack configuration for resistive random access memory (ReRAM) application. Excellent bipolar resistive switching (RS) properties have been observed at a low voltage of +2.1 V and -2.5 V respectively, which favors device to reduce the power consumption. The advantages of employing WN over Pt or Ti as bottom electrode material were demonstrated such as the low resistive state value and uniformity of other RS parameters like endurance and retention. Formation/disruption of the conducting filament is verified as the main cause of exhibiting the RS properties. Ohmic behavior and trap-controlled space charge limited current (SCLC) conduction mechanisms are confirmed as dominant conduction mechanism at low resistance state (LRS) and high resistance state (HRS). High resistance ratio (10^2) corresponding to HRS and LRS, good write/erase endurance (10^3) and non-volatile long retention (10^3 sec) are also observed. This study demonstrated that the MoS_2 thin films with WN bottom electrode have a great potential for future non-volatile ReRAM application.

Author Index

Bold page numbers indicate presenter