Spectroscopic Ellipsometry Focus Topic
Room: 112 - Session EL+EM+EN-ThM

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches
Moderator: Tino Hofmann, University of Nebraska - Lincoln, Vimal Kamineni, Globalfoundries, Ny, Usa

8:00am **EL+EM+EN-ThM1 Multi-Spectral Polarimetric Imaging and Biomedical Applications**, ***Bernard Drevillon***, *A. Pierangelo*, LPICM-CNRS, Ecole Polytechnique, France **INVITED**

In the last years Polarimetric Imaging has received considerable attention in the literature thanks to its tremendous potential for the assessment of biological tissues in biomedical diagnostics. Light Polarization allows obtaining morphological information on tissues microscopic structure, potentially improving the diagnosis and treatment of several pathologies. Moreover, polarimetric imaging can be implemented using conventional light sources, like LED or halogen lamps, making it a cheap alternative to current standards. For several years the PICM Laboratory has designed and built innovative polarimetric imagers for biomedical applications. In particular, the development of the *eigenvalue calibration method* [1], led to the design of several polarimeters for macroscopic and microscopic analysis (in real and Fourier space) of *ex vivo* samples and for *in vivo* diagnoses. The development of such new instruments ranged from the simple measurement of polarization degree to the complete Mueller polarimetry. Several studies were devoted to the early detection and staging of uterine cervix cancer and to show that polarimetric imaging is effective for the visualisation and first grading of cervical dysplastic regions for patients with anomalous Pap smear [2]. Mueller matrix imaging polarimetry also provides enhanced contrast to differentiate types of cancer of colon and their stage of progress and penetration, which is currently detectable only by histological examination [3]. Moreover, this technique may also be useful to quickly verify the presence of residual cancer in the rectum after treatment with radiochemotherapy [4]. Finally, as a complementary development to experimental techniques, the set-up of Monte-Carlo detailed modelling of polarized light scattering in tissues has been carried out in the last few years and provides fundamental insight on the origin of observed polarimetric contrasts [5]. In conclusion the synergy of new experimental techniques based on polarimetry with the biomedical analysis and theoretical computer models, led to significant advances in the field of biological tissues characterization and diagnosis of related pathologies.

[1] E. Compain et al., Appl. Opt. 38, 3490-3502 (1999).

[2] A. Pierangelo et al., Opt. Express, 21, 14120 -14130 (2013).

[3] A. Pierangelo et al., Opt. Express 19, 1582 (2011).

[4] A. Pierangelo et al., J. Biomed. Opt., 18 (04), 046014 (2013).

[5] M.R. Antonelli et al., Opt. Express 18, 10201 (2010).

8:40am **EL+EM+EN-ThM3 Anisotropic Optical Properties of Rhombohedral and Tetragonal $BiFeO_3$ Phases**, ***Daniel Schmidt***, National University of Singapore, *L. You,* Nanyang Technological University, Singapore, *X. Chi,* National University of Singapore, *J. Wang,* Nanyang Technological University, Singapore, *A. Rusydi*, National University of Singapore

Single crystalline bismuth ferrite ($BiFeO_3$) is a multiferroic perovskite structure and exhibits magnetic as well as strong ferroelectric behaviour at room-temperature. Since about a decade $BiFeO_3$ is of strong research interest due to its potential applicability in ferroelectric memory devices and spintronics, for example [1].

While the lattice system of bulk $BiFeO_3$ is rhombohedral, the crystal structure of thin films can be engineered by introducing epitaxial strain. Depending on the choice of single crystalline substrate materials the thin film $BiFeO_3$ crystal structure and associated physical properties can be modified.

Here, we present the anisotropic optical properties of high-quality multiferroic $BiFeO_3$ thin films determined with Mueller matrix ellipsometry at room-temperature within the spectral range of 0.6 and 6.5 eV. The full dielectric function tensors of tetragonal-like and rhombohedral-like $BiFeO_3$ phases epitaxially grown on $LaAlO_3$ and $SrTiO_3$ single crystal substrates, respectively, are discussed. Significant birefringence and dichroism are observed as well as strain-induced differences in critical point energies between both phases.

The importance of careful optical analysis of anisotropic Mueller matrix data will be discussed, which allows for characterization of subtle sub-band gap crystal field transitions and reveals indications of an indirect band gap. Such transitions have been observed before by means of other techniques but not by ellipsometry. Additionally, the analysis of Mueller matrix data revealed that an unintentional substrate miscut can introduce an overall polarization tilt of the ferroelectric thin films. This tilt was confirmed by extensive in- and out-of-plane piezoelectric force microscopy studies.

An accurate determination of the dielectric function tensor is of high importance to verify or, if necessary, improve and correct ab-inito calculations, which are crucial for understanding the driving physical principles in such complex materials. A comparison of the experimental results with state-of-the art first-principle calculations will be presented.

[1] G. Catalan and J.F. Scott, Adv. Mater. 21, 2463 (2009).

9:00am **EL+EM+EN-ThM4 Temperature Dependent Structural and Optical Properties of SnO_2 Thin Film**, ***Junbo Gong***, *R.C. Dai, Z.P. Wang, Z.M. Zhang, Z.J. Ding*, University of Science and Technology of China

SnO_2, which is an n-type semiconducting material with a wide band gap 4 eV, is an interesting material due to its high electrical conductivity and optical transparency. SnO_2 film is attractive for many applications such as optoelectronic devices, gas sensors, thin film transistors, transparent electrodes, anti-reflecting coating, and as catalyst support.

In this work, the ellipsometric parameters of SnO_2 films on quartz glass are measured by spectra ellipsometer(J. A. Woollam M-2000U) in the wavelength range of 300 to 1000 nm at different temperature from room temperature to 600 ^oC. By using a semitransparent model, the precise thickness and optical constants of SnO_2 thin film depending on the temperature were obtained and the evolution process was studied. The film thickness significantly decreased with increased temperature from 100 ^oC to 300 ^oC and the absorption edge has an obvious blue shift which means an increased band gap. The result reveals that this process is not reversible. Combined with XRD measurement, we identified that the change of thickness and optical properties of SnO_2 film was due to a phase transition from rutile structure to columbite structure.

9:20am **EL+EM+EN-ThM5 Determining Curvature Radius of a Curved Surface by use of Mueller Matrix Ellipsometry**, ***Weiqi Li***, *H. Jiang, C.W. Zhang, X.G. Chen, S.Y. Liu*, Huazhong University of Science and Technology, China

Determining curvature radius of a curved surface by use of Mueller matrix ellipsometry

Weiqi Li, Hao Jiang, Chuanwei Zhang, Xiuguo Chen, and Shiyuan Liu*

State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, China.

* Corresponding author: shyliu@hust.edu.cn

Ellipsometry is a powerful metrology tool for the characterization of surfaces and thin films. Generally, the basic principle of conventional ellipsometry is based on the assumption that the studied film or structure is on a planar surface [1], in another word, the conventional ellipsometry works the best for a flat surface. When the studied surface is tilted or curved, the measurement accuracy of the conventional ellipsometry will be significantly degraded, or even be incorrect. It is thus important to develop a method to deal with the cases when the surface for characterization is tilted or curved. Comparing with the conventional ellipsometry, the Mueller matrix ellipsometry (MME) can provide all 16 elements of a 4 by 4 Mueller matrix, and consequently can acquire much more useful information about the curved surface and thereby shows great potential in the curved surface metrology.

In this work, we propose an optical model that is able to process curved surface based on our in-house developed dual rotating-compensator MME [2] to characterize the surface layer of a single crystal silicon sphere crown with a radius of about 51 mm for demonstration. Focus probe accessory is used in the MME to achieve sufficient small spot on the curved surface so that the detected area on the spherical surface can be approximately regarded as a tilted one. We found that some of the measured off-diagonal Mueller matrix elements are very sensitive to the offset between the actual detected spot and the surface vertex, which is proportional to the deviation angle α of the surface normal across the surface vertex. An optical model of the spherical layer is proposed by considering the curved surface of the silicon sphere crown and the offset. With the proposed model, the deviation angle α as well as the surface layer thickness can be extracted from the measured Mueller matrix spectrum, and then the curvature radius of the sphere crown can be achieved. Experiments are performed on the silicon sphere crown show that not only the accuracy of measurement can be improved but also the curvature radius of the sphere crown is capable to be measured using the proposed optical model.

[1] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, 1992).

[2] S. Y. Liu, X. G. Chen, and C. W. Zhang, *Thin Solid Films* **584**, 176-185 (2015).

9:40am **EL+EM+EN-ThM6 Cavity-Enhanced Optical Hall Effect in AlInN/GaN-based HEMT Structures Detected at Terahertz Frequencies**, ***Sean Knight***, University of Nebraska-Lincoln, *S. Schöche,* J.A. Woollam Co. Inc., *V. Darakchieva, P. Kühne,* Linköping University, Sweden, *J.-F. Carlin, N. Grandjean,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *C.M. Herzinger,* J.A. Woollam Co. Inc., *M. Schubert, T. Hofmann*, University of Nebraska-Lincoln

The terahertz optical Hall effect (THz-OHE) has been established as a non-contact and therefore valuable tool for the investigation of free charge carrier properties in semiconductor heterostructures [1-4]. In this work, we demonstrate that the THz-OHE signal for samples grown on THz transparent substrates can be controlled and enhanced by a tunable, externally coupled Fabry-Pérot cavity mode [5]. An AlInN/GaN-based high electron mobility transistor structure (HEMT) grown on a sapphire substrate is investigated as an example, while the cavity enhancement phenomenon discussed here is generally applicable to situations when a layered sample is deposited onto a THz transparent substrate. We show that in the vicinity of an externally coupled-cavity mode, a strong enhancement of the OHE signatures of up to one order of magnitude can be achieved by optimizing the cavity geometry, which is very useful for small magnetic field strengths. This signal enhancement allows the determination of free charge carrier effective mass, mobility, and density parameters using OHE measurements in low magnetic fields. Previously, high-field electromagnets needed to be employed for THz-OHE measurement for the determination of free charge carrier parameters in semiconductor heterostructures. Tuning the external cavity allows an enhancement of the THz-OHE signatures by as much as one order of magnitude. We propose to employ this enhancement effect to reliably and accurately determine free charge carrier properties in semiconductor structures at small magnetic fields dispensing with the need for expensive high magnetic fields. Cavity-enhanced THz-OHE may therefore enable the wide spread contactless measurement of free charge carrier properties at THz frequencies and which is indispensable for the development of the next generation of group-III nitride-based high frequency devices.

11:00am **EL+EM+EN-ThM10 Biosensor based on Imaging Ellipsometry and its Biomedical Applications**, *Y. Niu*, ***Gang Jin***, Institute of Mechanics, Chinese Academy of Sciences, China **INVITED**

The concept of biosensor based on imaging ellipsometry (BIE) was proposed in 1995 [1, 2]. With the development in recent 20 years, it has been formed an automatic analysis technique for detecting biomolecule detection interaction with merits of rapid, label-free, quantitative, high throughput and real-time. Its principle, methodology, biosensor system and biomedical applications are reviewed in this report.

A BIE system can be divided into four parts: the microfluidic array reactor, the imaging ellipsometer, the control system, and the biosensor database. The microfluidic array reactor serves to fabricate the protein microarray and accommodate biomolecular interactions. Using the microfluidic array reactor, various ligands are immobilized to different cells to form a sensing array, and each sensing surface can be prepared homogeneously under the flow condition. The imaging ellipsometer acts as a reader for data acquisition from the microarray. Since imaging ellipsometry is sensitive to slight variations of optical thickness, it can be used to visualize ultra-thin films and the change of molecular mass surface concentration. The control system combines the reactor with the imaging ellipsometer and functions to control the hardware's mechanical motion and obtain results in images, while the biosensor database is to aid BIE users in determining optimized experimental conditions and comparing previous test data.

The sensitivity and flexibility of the biosensor is very important for practical purpose, especially in biomedical fields. The sensitivity depends not only upon the resolution of imaging ellipsometry but also upon the bio-system of ligand-receptor on the microarray that is the bioactivity and its act related to the ligand screen, ligand immobilization, unspecific blocking and interaction conditions, etc. The flexibility mainly depends on the mechanical, electrical, informatics and biological control. So far, a serviceable engineering system of the biosensor and some bio-systems is installed available for more applications, especially for high throughput protein analysis, such as antibody screening [3], disease markers serological detection [4] and joint detection of tumor markers [5] as well as virus infection identification [6-7].

References

[1] G. Jin, et al., *Anal. Biochem.* **232**, 69 (1995).

[2] G. Jin, R. Jansson, and H. Arwin, *Rev. Sci. Instrum.***67**, 2930 (1996).

[3] Y. Niu, et al., *Thin Solid Films***519** 2768 (2011).

[4] C. Qi, et al., *J. Viral Hepatitis***16**, 822 (2009).

[5] Y. Niu , et al., *Thin Solid Films***571**, 453 (2014).

[6] C. Qi, et al., *Biosensors & Bioelectronics***25**, 1530 (2010).

[7] C. Qi, et al., *Virus Res.***140**, 79 (2009).

11:40am **EL+EM+EN-ThM12 Screening Breast Cancer by Joint Detection of Tumor Marker Carbohydrate Antigen 15-3 and Carbohydrate Antigen 242 with Biosensor Based on Imaging Ellipsometry**, ***Yu Niu***, *G. Jin*, Institute of Mechanics, Chinese Academy of Sciences, China

Breast cancer which develops from breast tissue is the leading type of cancer in women worldwide, accounting for more than 25% of all carcinogenesis [1]. Compared with other common cancers, the survival rate of breast cancer is remarkably positive and optimistic that between 80% and 90% of those in developed country could be alive for at least 5 years. Therefore, screening high risk population and further concluding a clinical diagnosis in the early stage act as a pivotal factor to cure breast cancer, because it can provide overwhelming contribution to carry out essential therapy in time. Carbohydrate Antigen 15-3 (CA 15-3) and Carbohydrate Antigen 242 (CA 242) are widely-used tumor markers for breast cancer in clinic and their concentrations in serum vary sensitively with breast cancer genesis. The biosensor based on imaging ellipsometry (BIE) for visualization of biomolecular interactions was reported in 1995 [2] and now it is composed of a 48 protein unit array and imaging ellipsometry reader with a field of view (20 x 30 mm) and good resolution for protein adsorption layer on a silicon substrate (lateral and vertical is 1 μm and 0.1 nm, respectively) [3]. In this investigation, joint detection of these two tumor markers simultaneously has been performed with BIE as a trial for screening breast cancer for clinical purpose.

To realize the joint detection, a series of design and optimization has been performed, including the ellipsometric setting, ligand immobilization strategy, ligand surface density, as well as the blocking and rinsing procedures. The test concentration range calibration and the detection limit for quantitative detection have been established by standard samples, which meet the standards of clinical test. By diluting sera to the detection range fitting to the calibration curves, joint quantitative detection of CA 15-3 and CA 242 can be achieved simultaneously.

149 serum samples composed of both the healthy and patients have been performed with BIE. Compared with the results obtained by standard approaches in clinic, the correlation analysis indicates the BIE are highly consistent with clinical methods. In order to estimate the BIE performance for tumor markers detection, ROC curve analysis has been introduced. Its result suggests that the single marker detection by BIE presents good capability to distinguish the normal from patients and the joint detection of CA 15-3 and CA 242 plays a positive role in the improvement of the diagnosis specificity and accuracy.

Reference

[1] A. Jemal, et al., *CA Cancer J. Clin.***61**, 69 (2011).

[2] G. Jin, et al., *Anal. Biochem.***232**, 69 (1995).

[3] G. Jin, et al., *Thin Solid Films***519,** 2750 (2011).

12:00pm **EL+EM+EN-ThM13 Decomposition of Angle Resolved Spectroscopic Mueller Matrices from Scarabaeidae Beetles**, ***Roger Magnusson***, Linköping University, Sweden, *R. Ossikovski, E. Garcia-Caurel,* LPICM-CNRS, Ecole Polytechnique, France, *K. Järrendahl, H. Arwin*, Linköping University, Sweden

We use angle-dependent Mueller-matrix spectroscopic ellipsometry (MMSE) to determine Mueller matrices of Scarabaeidae beetles which show fascinating reflection properties due to structural phenomena in the exocuticle which are often depolarizing. It has been shown by Cloude [1] that a depolarizing matrix can be decomposed into a sum of up to four non-depolarizing matrices according to $\mathbf{M}= a\mathbf{M}_1+b\mathbf{M}_2+c\mathbf{M}_3+d\mathbf{M}_4$, where a, b, c and d are eigenvalues of the covariance matrix of **M**. Using the same eigenvalues the matrices $\mathbf{M}_i$ can be calculated. This method provides the full solution to the decomposition with both the non-depolarizing matrices and the weight of each of them in the sum.

An alternative to Cloude decomposition is *regression decomposition*. Here any Mueller matrix can be decomposed into a set of matrices $\mathbf{M}_i$ which are specified beforehand. Whereas in Cloude decomposition the only constraint on the matrices is that they are physically realizable non-depolarizing Mueller matrices, we can now limit the constraint and only use Mueller matrices representing pure optical devices having direct physical meaning, such as polarizers, retarders, etc. This leaves a, b, c, d as fit parameters to minimize the Frobenius norm $\mathbf{M}^{exp}$ -$\mathbf{M}^{reg}$ where $\mathbf{M}^{exp}$ is the experimentally determined Mueller matrix to be decomposed and $\mathbf{M}^{reg}$ is the sum of all $\mathbf{M}_i$. Depending on $\mathbf{M}^{exp}$ an appropriate choice of $\mathbf{M}^{reg}$ matrices has to be made and different values of a, b, c and d are obtained through regression analysis.

We have previously shown that regression decomposition can be used to show that the Mueller matrix of *Cetonia aurata* can be decomposed into a sum of a circular polarizer and a mirror [2]. Here we expand the analysis to include angle-resolved spectral Mueller matrices, and also include more species of Scarabaeidae beetles.

One effect of the decomposition is that when depolarization is caused by an inhomogeneous sample with regions of different optical properties the Mueller matrices of the different regions can be retrieved under certain conditions. Regression decomposition also has potential to be a classification tool for biological samples where a set of standard matrices are used in the decomposition and the parameters a, b, c, d are used to quantify the polarizing properties of the sample.

[1] Cloude S.R. 1989. Conditions for the physical realisability of matrix operators in polarimetry. Proc. SPIE 1166, Polarization Considerations for Optical Systems II, pp. 177-185

[2] Arwin H, Magnusson R, Garcia-Caurel E, Fallet C, Järrendahl K, De Martino A, Ossikovski R, 2015. Sum decomposition of Mueller-matrix images and spectra of beetle cuticles. Opt. Express, vol. 23, no. 3, pp. 1951–1966

Spectroscopic Ellipsometry Focus Topic
Room: 112 - Session EL+AS+BI+EM-ThA

Optical Characterization of Nanostructures and Metamaterials
Moderator: Bernard Drevillon, LPICM-CNRS, Ecole Polytechnique, France, Mathias Schubert, University of Nebraska - Lincoln

2:20pm **EL+AS+BI+EM-ThA1 Electrostatic Coating with Ligandless Copper Nanoparticles**, ***Lance Hubbard***, *A.J. Muscat*, University of Arizona

Electroless deposition (ELD) produces conformal coatings at low temperatures. ELD occurs by chemical reduction of metal ions without an externally applied potential or catalyst layer. In this paper, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) native oxide was hydroxylated and terminated with a self-assembled amine layer (4 mM (3-aminopropyl)-trimethoxysilane in methanol). Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol (reducing agent), and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The Cu particle ion shell is attracted to the positively charged amine groups at high pH depositing a thin metal film that is both continuous and cohesive. Annealing the coupons at 200^{o}C in nitrogen promoted electrically conductive film formation. Electron microscopy images of the coated substrates showed a 80-95 nm thick film of 3 nm diameter particles. Four-point probe measurements of the films yielded electrical conductivities in the range 10^{6}-10^{7} S/m (10-80% of bulk conductivty). The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.56 nm. Scanning electron microsopy (SEM) images at various angles in relation to the films were taken to examine film morphology and thickness. Spectroscopic ellipsometry (SE) data were modelled with bulk, nanophase d-band transition, and SPR absorbances. The SE agreed well with UV-VIS results for the SPR and shows an increasing contribution from d-band transitions with increasing ionic liquid concentration. SEM and Fourier transform infrared (FTIR) spectroscopy were used to determine film thicknesses and chemistry.

2:40pm **EL+AS+BI+EM-ThA2 Using Plasmonic Effects to Design Ellipsometric Targets with Sub-Angstrom Resolution**, ***Samuel O'Mullane***, SUNY Polytechnic Institute, *J. Race, N. Keller,* Nanometrics, *A.C. Diebold*, SUNY Polytechnic Institute

For traditional ellipsometric targets, slightly changing the thickness of a layer or the index of refraction of a material results in a similarly small change in the observed spectra. If structures are designed to allow for plasmonic coupling, a slight change in those same parameters results in wildly different spectra. Specifically, localized plasmonic resonances in metallic grating structures allow for extraordinary sensitivity to parameters such as CD, sidewall angle and pitch.

Existing metallic grating structures are arrays of long, thin lines of copper that can be described using one dimension. The typical resolution for ellipsometric CD measurements on these structures ranges from nanometers to Ångströms. Because there is no confining second dimension, localized plasmons cannot be produced.

In order to obtain sub-Ångström resolution, additional structural modifications are required. This is achieved by adding a second metallic grating perpendicular to the original grating forming a cross-grating structure. Note that the added pitch and linewidth are an order of magnitude larger than the original parameters. This results in fully localized plasmonic resonances so that parameter variation on the order of tens of picometers could be detected through ellipsometric measurements. Making use of conical diffraction further increases the sensitivity to structural changes due to increased anisotropy.

These conclusions are the result of rigorous coupled wave-analysis (RCWA) simulations which were confirmed via finite element method (FEM) simulations. With both RCWA and FEM agreement, experimental confirmation is expected.

3:00pm **EL+AS+BI+EM-ThA3 Enhanced Temperature Stability of Slanted Columnar Thin Films by ALD Overcoating**, ***Alyssa Mock***, *D. Sekora, T. Hofmann, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

The demand for thermally stable nanostructures continues to increase as nanotechnology becomes ever more prevalent in both commercial and research applications. The high surface area of nanostructured thin films is susceptible to degradation under extreme temperatures. Scanning electron microscopy (SEM) and Mueller Matrix Generalized Ellipsometry (MMGE) were used to observe optical and structural properties of a glancing angle deposited cobalt slanted columnar thin film (SCTF) over increased annealing temperature. We show that the use of atomic layer deposition (ALD) to conformally passivate the SCTF surface provides both physical scaffolding and thermal protection during the annealing process up to 475°C as no changes in the SEM or MMGE results were present.

3:20pm **EL+AS+BI+EM-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Heat Treated Sculptured Thin Films: A Study of the Effects of Al_2O_3 Passivation Coatings on Magneto-Optical Properties**, ***Chad Briley***, *A. Mock,* University of Nebraska-Lincoln, *D. Schmidt,* National University of Singapore, *T. Hofmann, E. Schubert, M. Schubert*, University of Nebraska-Lincoln

We present the vector magneto-optical generalized ellipsometric (VMOGE) response[1] and model dielectric function (MDF) anisotropic hysteresis calculations[2] of ferromagnetic slanted columnar thin films under the effects of heat treatment up to 475° C. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on Cobalt slanted columnar thin film samples grown by glancing angle deposition with and without Al_2O_3 conformal passivation overcoating done by atomic layer deposition. Analysis of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determine the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor displays anisotropic magnetic response of the thin film with the hard axis along the long axis of the columns. Data analysis reveals the preservation of anisotropic magneto-optical properties of the thin film with the passivated coating as compared to the non-passivated coating due to oxidation effects from heat treatment.

[1)] D. Schmidt, C. Briley, E. Schubert, and M. Schubert, Appl. Phys. Lett. **102**, 123109 (2013).

[2)] C. Briley, D. Schmidt, T. Hofmann, E. Schubert, and M. Schubert, Appl. Phys. Lett. **106**, 133104 (2015).

4:00pm **EL+AS+BI+EM-ThA6 Spectroscopic Ellipsometry for Critical Dimensions Analysis**, ***Vimal Kamineni***, GLOBALFOUNDRIES, *D. Dixit, S. O'Mullane,* SUNY Polytechnic Institute, *G. Iddawela, A. Vaid,* GLOBALFOUNDRIES, *A.C. Diebold*, SUNY Polytechnic Institute **INVITED**

In this talk an overview of the current applications of spectroscopic ellipsometry (SE) towards measuring the shape of nanostructures will be presented. The transition of the semiconductor industry from planar to 3D transistors has expanded the applications of ellipsometry. Ellipsometry measurements on the periodic nanoscale structures enable a diffraction based measurement technique referred to as scatterometry. The critical dimensions can be extracted by means of a regression on the diffracted light using rigorous coupled wave analysis (RCWA). RCWA is a Fourier-space method used to generate the optical response by slicing the periodic structure of interest and matching the boundary conditions to compute EM modes. This method is inherently dependent on *a priori* knowledge of the dielectric function of the materials that construct the nanostructures as well as the shape of the nanostructure obtained from reference metrology. Furthermore, time-to-solution is one of the main drawbacks of developing scatterometry applications due to the dependency on developing a robust model and for validating the model with reference metrology measurement. To address these challenges new methods such as signal response metrology (SRM) encompassing machine-based statistical learning and virtual reference metrology have been proposed. [1,2] These methods will be reviewed along with their benefits and limitations when applied to advanced 3D transistor structures. In addition, application of Mueller matrix ellipsometry measurements on strained grating structures (SiGe/Si) and block copolymer structures to determine the impact of strain and defectivity (bridging defects, wiggles, LER, etc.) on anisotropy coefficients will be presented, respectively. [3,4] Additionally, hybrid approaches will be proposed in conjunction with complementary/supplementary metrology methods (CD-SEM, HRXRD and CD-SAXS). [5-7]

[1] S. Pandev et al., SPIE Proc. 9424 (2015).

[2] A. Vaid et al., SPIE Proc. 9424 (2015).

[3] G. R. Muthinti et al., SPIE Proc. 8681 (2013).

[4] D. J. Dixit et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 14, 021102 (2015).

[5] A. Vaid et al., SPIE Proc. 8324 (2012).

[6] A. C. Diebold et al., Proceedings of SPIE 8681, 86810I (2013).

[7] Charles Settens et al., Journal of Micro/Nanolithography, MEMS, and MOEMS 13, 041408 (2014)

4:40pm **EL+AS+BI+EM-ThA8 Structural and Ellipsometric Analysis of the Topological Insulator Bi_2Se_3**, ***Avery Green***, SUNY Polytechnic Institute

Topological Insulator (TI) materials have been the subjects of increasing scientific interest in the last decade. Their spin-momentum locked Dirac cone surfaces and insulating bulks have resulted in new directions in physics research and new spintronic devices. Though these materials have been thoroughly described in theory, the experimental realization and measurement of these surface states has been problematic, due to various crystalline defects. Theory predicts that TI surface states are protected against local defects, but it is essential to study the effects of global perturbations caused by surface oxidation, stoichiometric aberrations, and significant structural defect densities. The aim of this study is to measure the time-dependent dielectric function of the Bi_2Se_3 surface and bulk in air, using a dual rotating compensator spectroscopic ellipsometer. These data are backed up with various metrological measurements (AFM, cross-sectional TEM, EDS) to confirm surface topology and oxide thickness. This analysis of optical properties and oxide formation will, in the future, be used to optimize the Bi_2Se_3 flake thickness identification process, and provide a control for further necessary structural analysis, as stated above.

5:00pm **EL+AS+BI+EM-ThA9 Visible Luminescence in the VLS Grown Self Ga Doped ZnS Nanostructures**, ***Arshad Bhatti****, H. Hussain, M.A. Johar, S. Rehman, M.A. Shehzad, M.A. Hafeez*, COMSATS Institute of Information Technology, Pakistan

ZnS is a wide band gap semiconductor and thus offers fascinating opportunities for tailoring and tuning its bandgap states for photonic devices in visible region of the spectra. Ga introduced a strong red luminescence in ZnS. VLS mechanism was employed to synthesize ZnS nanowires using Ga as a catalyst and dopant simultaneously. The thickness of Ga ultrathin film was varied from 0.5 nm to 5 nm to observe the effect of Ga droplet size on the formation, lifetime and activation energies of defect states in the band gap. It was expected that Ga^{3+} would replace Zn^{2+} sites and dope ZnS, in addition, an impurity phase of Ga_2S_3 was also observed, whose content showed strong dependence of Ga thickness. It also shrunk the crystallinity of ZnS due to varied size of Ga^{3+}(76 pm) ions replacing Zn^{2+} (88 pm), which was observed in the shifts of major XRD reflections of ZnS. Incorporation of Ga introduced strong impurity states in the band gap of ZnS. It also affected the intrinsic defect states of ZnS, namely Zn and S vacancies (Please refer to Figure 1, which also shows the de-convoluted band gap broad band). In the PL spectra, blue (440 nm), yellow (560 nm), orange (600 nm) and red (680 nm) bands were attributed to S vacancies, Ga related defects, donor-acceptor recombination and Ga_2S_3, respectively. Photoluminescence excitation spectroscopy revealed strong absorbance at corresponding energies. A strong correlation of these states was observed in the temperature dependent PL measurements due to presence in their presence in the vicinity as the activation energies of these states matched the energy differences of corresponding states. The conductivity measurements also complimented the optical results. Time resolved PL demonstrated the lifetime of these states was between 0.5 ns to 1.5 ns and had somewhat significant effect of dopant concentration. Finally, Ga doped ZnS showed extremely efficient IR sensitivity.

Figure 1: The room temperature PL spectra of Ga doped ZnS nanowires synthesized with varied thickness of Ga: (a) 0.5 nm, (b) 1.0 nm, (c) 3.0 nm, and (d) 5.0 nm. The broad band between 450 nm to 750 nm has been de-convoluted to show contribution of various defect states (as mentioned in the Figure). These states were identified from the PLE spectrum.

5:40pm **EL+AS+BI+EM-ThA11 Can Front-Surface Metal Mirrors Be Protected from Oxidation by Vacuum Applied Polymer Films?**, ***David Allred****, R.S. Turley,* Brigham Young University*, R.T. Perkins*, Utah Valley University

We have used variable-angle, spectroscopic ellipsometry to monitor secular changes in multilayers consisting of chemically active thin films, such as aluminum, deposited on dielectric-coated silicon wafers and protected by various vacuum-applied barrier layers. Ultrathin barrier layers included polymers such as parylene and rarely, sputtered inorganic films, such as silicon. Applications include the measurements of the oxidation of evaporated aluminum for use as a mirror in the VUV (vacuum ultraviolet) and the determination of the optical constants of materials such as Y_2O_3 potentially useful in VUV and XUV (extreme ultraviolet) optics.

Spectroscopic Ellipsometry Focus Topic
Room: Hall 3 - Session EL-ThP

Spectroscopic Ellipsometry Poster Session

EL-ThP2 Phonon Dispersion and Electronic Band Structure of NiO, ***Stefan Zollner****, A. Ghosh, T. Willett-Gies,* New Mexico State University*, C. Nelson,* University of New Mexico*, L. Abdallah*, New Mexico State University

The phonon dispersion and the electronic band structure of bulk NiO were investigated at 300 K using spectroscopic ellipsometry from the mid-infrared (0.03 Ev) to the near-ultraviolet (6.5 Ev). Since NiO crystallizes in the rocksalt structure, we find a single transverse-optical (TO) phonon at 49 meV with a broadening of 2 meV. There is no evidence of mode-splitting (due to antiferromagnetic ordering, within the broadening of this phonon of 2 meV) or zone folding (due to the doubling of the unit cell). Instead, we find a modification of the reststrahlen band due to TA+TO two-phonon absorption occurring between the TO and LO phonon energies, similar to LiF. Using transmission and ellipsometry measurements, we clearly establish that the lowest direct band gap of NiO occurs at 0.85 Ev at room temperature. The valence band maximum (VBM) of NiO is made up of O (2p) states and the lower Hubbard band of the Ni (3d) states. Direct interband transitions at 0.85 Ev are possible from the valence band to the dispersive Ni (4s) conduction band at the Γ point. A strong peak in the absorption at 3.95 Ev is attributed to transitions from the valence band to the upper Hubbard band (the charge transfer gap of NiO). A derivative analysis of the ellipsometry spectra also shows weak peaks at intermediate energies (between 1.7 and 3.6 Ev), which are attributed to transitions from localized valence band states to the dispersive Ni (4s) band. The charge-transfer gap of NiO shows a temperature dependence very similar to the E_1 gap of Si. The absorption between 1 and 3 Ev has a very different behavior, however. The character of the pseudo-dielectric function of NiO changes completely between 700 and 800 K in UHV, where NiO is known to deteriorate due to sublimation. Cooling the sample does not restore the original shape of the dielectric function, but it can be recovered partially by annealing in oxygen.

EL-ThP3 Tribrid EC-QCMD-GSE Analysis: Surface Topography Effects on the Electrochromic Behavior of Methylene Blue, ***Derek Sekora****, A.J. Zaitouna, R.Y. Lai, T. Hofmann, M. Schubert, E. Schubert*, University of Nebraska - Lincoln

The optical and electrical properties of flat and highly ordered, 3-dimensional nanostructured thin films change dramatically upon adsorption of self assembled monolayers (SAMs) to the surface. Here, a tribrid technique consisting of electrochemistry (EC), quartz crystal microbalance with dissipation (QCM-D), and generalized spectroscopic ellipsometry (GSE) is introduced which allows for fundamental analysis of simultaneous electrochemical, optical, and mechanical properties. The electrochromic reduction of methylene blue terminated SAMs on flat and slanted columnar thin film Au substrates is investigated as an example.

The electrochemical redox reaction of methylene blue produces a switch between a blue and colorless SAM, which can be ellipsometrically modeled. Furthermore, a combinatorial tribrid analysis of in-situ step-decreased constant potential scans elucidate the effects of varying the quantity of reduced methylene blue molecules on flat and nanostructured surfaces. The EC and GSE results imply that methylene blue molecules attached deep between Au slanted columns are not as readily reduced as a result of capacitive shielding effects at lower cell potentials. The concurrent in-situ QCM-D response indicates no quantifiable mass transfer as expressed by the Sauerbrey analysis. The results demonstrate that the fluidic tribrid technique allows characterization of conformal coatings on highly ordered nanostructured surface topographies during electrochemical surface modifications. Our approach is perfectly suited for applications including DNA sensing procedures, electrochemical surface reactions, and surfactant effects.

Authors Index

Bold page numbers indicate the presenter