

Spectroscopic Ellipsometry Focus Topic Room A212 - Session EL+AS+EM+TF-WeM

Optical Characterization of Thin Films and Nanostructures

Moderators: Eva Bittrich, Leibniz Institute of Polymer Research Dresden, Tino Hofmann, University of North Carolina at Charlotte

8:00am **EL+AS+EM+TF-WeM-1 Enhanced Strong Near Band Edge Emission from Lanththanide Doped Sputter Deposited ZnO**, *C Heng*, Beijing Institute of Technology, China; *W Xiang, T Wang*, Beijing Institute of Technology, China; *W Su*, Beijing Institute of Technology, China; *P Yin*, Beihang University, China; *Terje G Finstad*, University of Oslo, Norway
Research on ZnO films and nanostructures have increased steadily in the last decades being motivated by many applications including photonic applications. Incorporation of rare earth (RE) elements for the purpose utilize transition therein for conversion or manipulation of the wavelength spectrum. That was also our original motivation, however we observed the REs also can provide an enhancement of near band gap emission, NBE. This has been observed for Tb, Ce, Yb and Eu. The ZnO films were co-sputtered with RE elements onto Si wafers in an Ar+O₂ ambient yielding oxygen rich films as observed by RBS and XPS. The films were annealed in an N₂ ambient for various temperatures from 600 to 1100 °C. The luminescence behavior was studied emission and excitation spectroscopy as well luminescence decay measurements. Both undoped and RE doped films showed a large increase in emission with increasing annealing temperature, while the increase was largest for the RE doped samples. The crystallinity and microstructure of the films were studied by XPS, SEM, XRD and HRTEM. It is observed that the increase in UV NBE is correlated with crystalline improvements of ZnO. At the temperature for maximum PL emission intensity there is silicate formation due to interaction with the substrate. The maximum occurs for an annealing temperature where not all the ZnO has been consumed in the silicate reaction. This maximum appears to be 1100 °C for the thicker films and 1000 °C for thinner films. For samples having maximum NBE there seem to be random lasing occurring indicated by the intensity dependence of UV PL emission. A hypothesis for the main reason behind the increase in NBE intensity with RE doping is that the RE ions influence the film structure during nucleation early in the deposition process by influencing the mobility of atoms. The initial grain structure will have an affect on the development grain structure for the whole film and an influence on the grain growth. This influences the presence of non-radiative defect centers in the film and the grain surface and grain boundaries. As a side effect, we observe that there is very little transfer of excitation energy to the RE ions. This supports the notion that oxygen deficient centers may be necessary to have efficient energy transfer to RE ions in ZnO. Finally we remark that strong UV light from ZnO films have been sought particularly because they could offer a low temperature production for some application. The present method is still a high temperature method, but it is very simple and can be directly combined with Si technology which can be advantage for certain applications.

8:20am **EL+AS+EM+TF-WeM-2 Ellipsometry Study of PLD based Temperature Controlled Thin Film Depositions of CdSe on ITO Substrates**, *Flavia Inbanathan*, Ohio University; *M Ebdah*, King Saud University, Kingdom of Saudi Arabia; *P Kumar*, Gurukula Kangri Vishwavidyalaya, India; *K Dasari*, Texas State University; *R Katiyar*, University of Puerto Rico; *W Jadwisieniczak*, Ohio University

Cadmium Selenide(CdSe), a n-type semiconductor with a direct bandgap of 1.73eV has been explored widely for its suitability in various applications including photovoltaics and optoelectronics, because of its optical and electrical properties. The literature presents various deposition methods for CdSe thin films out of which this work is based on pulsed laser deposition(PLD)[1]. The optoelectronic applications of CdSe thin films depend on their structural and electronic properties that depends on deposition and process parameters[2]. The stability of the thin films at various temperatures is an important factor to improve the efficiency and durability of photosensitive devices. The present work aims to fabricate the high quality CdSe thin films using PLD method and affirms the optimal deposition temperature at 250°C as validated by the films surface roughness and ellipsometry studies[3][4]. The effect of different *in-situ* deposition temperature on structural, morphological and optical properties through XRD, AFM, SEM, optical absorption/transmission and ellipsometry spectroscopy have been investigated. CdSe thin films with thickness close to 200nm were deposited on the Indium Tin Oxide (ITO) coated glass

substrates at temperatures ranging from 150 to 400°C. The light absorption spectrum analysis of all the CdSe films confirmed well defined direct energy band gap from 2.03 to 1.83eV. The ITO substrate is modelled using a two sub-layers model that consists of 130nm graded ITO on top of a 0.7µm bulk ITO layer, and the experimental ellipsometry spectra agreed very well with the fitting spectra. The ellipsometry study confirmed that CdSe thin films show an increase of 44% in refractive index(*n*) in the violet spectrum, and a constant value in blue-yellow spectral range but with significant changes in red spectrum for increase in temperature upto 350°C; beyond which resulted in constant value, possibly due to the stagnation in the grain growth. The extinction coefficient(*k*) value of CdSe approaches zero in the red spectrum region for 150°C and 300°C temperatures whereas it showed a value of 0.25 and 0.7 for 250°C and 400°C temperatures, respectively. The peaks observed around 650nm and 750nm in ellipsometry spectra are assigned to excitonic transitions. The collected data will be critically analysed in terms of CdSe optical properties engineered for optoelectronic and photovoltaic applications.

References: [1]Z.Bao *et al.*, J.Mater.Sci.:Mater Electron(2016)27,7233-7239; [2]S.Mahato, *et al.*, J.Sci.: Adv.Mater. Devices, (2017)2,165-171; [3]A.Evmenova *et al.*, Advan. Mater. Scien.Eng. (2015), ID 920421,11; [4]B.T.Diroll *et al.*, Chem. Mater.,(2015)27,6463-6469.

8:40am **EL+AS+EM+TF-WeM-3 The Application of Mueller Matrix Spectroscopic Ellipsometry to Scatterometry Measurement of Feature Dimension and Shape for Integrated Circuit Structures**, *Alain C. Diebold*, SUNY Polytechnic Institute

INVITED

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. Here we use the structures used in GAA transistors fabrication as an example of challenging measurements.(1, 2, 3) In this talk, we present simulations aimed at understanding the sensitivity to changes in feature shape and dimension for the structures used to fabricate GAA transistors. Simulations of the multi-layer fins show a clear sensitivity to fin shape and Si layer thickness which is enhanced by the use of the full Mueller Matrix capability vs traditional spectroscopic ellipsometry. We also discuss experimental measurement of nanowire test structure demonstrating the ability to measure the etching of multiple sub-surface features. [3]

References

- [1] Alain C. Diebold, Anthony Antonelli, and Nick Keller, Perspective: Optical measurement of feature dimensions and shapes by scatterometry, *APL Mat.* **6**, (2018), 058201. doi: 10.1063/1.5018310.
- [2] Sonal Dey, Alain Diebold, Nick Keller, and Madhulika Korde, Mueller matrix spectroscopic ellipsometry based scatterometry simulations of Si and Si/SixGe1-x/Si/SixGe1-x/Si fins for sub-7nm node gate-all-around transistor metrology, *Proc. SPIE 10585*, Metrology, Inspection, and Process Control for Microlithography XXXII, 1058506 (6 June 2018); doi: 10.1117/12.2296988
- [3] Madhulika Korde, Subhadeep Kal, Cheryl Pereira, Nick Keller, Aelan Mosden, Alain C. Diebold, Optical Characterization of multi-NST Nanowire Test Structures using Muller Matrix Spectroscopic Ellipsometry (MMSE) based scatterometry for sub 5nm nodes, *Proc. SPIE Metrology, Inspection, and Process Control for Microlithography XXXIII*, (2019), in press.

9:20am **EL+AS+EM+TF-WeM-5 Optical Constants and Thickness of Ultrathin Thermally Evaporated Iron Films**, *Nick Allen, D Shah, R Vanfleets, M Linford, R Davis*, Brigham Young University

Carbon nanotube templated microfabrication (CNT-M) is a technique that uses a patterned iron catalyst to grow 3-D structures for device applications. Iron catalyst thickness strongly affects carbon nanotube (CNT) growth heights and the straightness of the CNT-M structures. Atomic force microscopy has been used to directly measure the thicknesses of such iron/iron oxide films, but this technique is slow and not easily scalable. A faster method is ellipsometry, but for very thin films, the optical constants and thickness are not easily separated, thus standard ellipsometry approaches are inadequate. The 2-6 nm thick iron films used as CNT growth catalysts are in this challenging region. The absorptive nature of the iron/iron oxide films adds further difficulty. In this study, a multi-sample ellipsometry analysis using iron films of various thicknesses was performed to obtain the optical constants of thermally evaporated iron. We used

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contrast enhancement by incorporating a silicon dioxide layer under the film being analyzed to enhance sensitivity to the optical constants.

9:40am **EL+AS+EM+TF-WeM-6 Birefringent Photonic Crystals for Polarization-discriminating Infrared Focal Plane Arrays**, *Marc Lata, Y Li, S Park, M McLamb, T Hofmann*, University of North Carolina at Charlotte
Infrared optical materials fabricated using direct laser writing have received substantial interest since the emergence

of this technology which is based on the two-photon polymerization of suitable monomers [1, 2]. We have

demonstrated that direct laser writing allows the fabrication of structured surfaces to reduce Fresnel reflection

loss in the infrared spectral range while two-dimensional photonic crystals enable optical filters with high spectral

contrast [3, 4]. In combination with the ability to fabricate large scale arrays of uniform structures, two-photon

polymerization could be a disruptive technology for enhancing focal plane arrays in IR imaging systems.

So far, photonic crystals which provide polarization selectivity have not been used for the pixel-based enhancement

of infrared focal plane arrays. Here we explore the form-birefringence found in photonic crystals composed

of arrays of subwavelength-sized slanted micro wires (Fig. 1) for this purpose. The photonic crystals investigated

here were fabricated in a single fabrication step using direct laser writing of an infrared transparent photoresist.

The lateral dimensions of the photonic crystals are comparable to the pixel size of infrared focal plane arrays which

is on the order of some tens of micrometers [5]. We observe a strong contrast under cross-polarized illumination

in the mid-infrared spectral range at $w = 1550 \text{ cm}^{-1}$. Finite-element-based techniques are used to optimized the

geometry of the constituents of the photonic crystals to minimize edge effects. We envision laser direct writing as

a suitable technique for the enhancement of focal plane arrays to enable focal-plane polarimeters for the infrared

spectral range.

11:00am **EL+AS+EM+TF-WeM-10 Relevance of hidden Valleys in the Dequenching of Room-temperature-emitting Ge Layers**, *T Sakamoto, Y Yasutake*, University of Tokyo, Japan; *J Kanasaki*, Osaka City University, Japan; *Susumu Fukatsu*, University of Tokyo, Japan

Ge offers a unique advantage of gaining a deeper insight into the intervalley coupling of *hot* electrons [1], which is arguably of importance in the context of controlling the optoelectronic and photonic functionalities [2]. In view of the complicated valley degeneracy in the near-band-edge region, such intervalley coupling of electrons plays a pivotal part even when strain-engineering pseudomorphic Ge-based quantum structures.

The capability of direct-gap emission at room temperature is of considerable practical significance of Ge, for which an added advantage is that emission wavelengths fortuitously fall within the telecom bands. Moreover, Ge is particularly interesting from the device physics point of view as it outperforms many semiconductor allies in the sense that thermal *dequenching* occurs near room-temperature: the emitted light intensity increases with increasing temperature, which is convenient but nevertheless logic-defying.

Such a rather counterintuitive “thermal roll-up”, as opposed to thermal roll-off which is usually more relevant, has been interpreted in terms of two-level electron kinetics assuming local thermal equilibrium; long-lived electrons populating the indirect conduction-band bottom, i.e., L-valleys, are excited up into the direct-gap Γ -valley by absorbing phonons, which seems to fit a fairly standard phenomenological picture reasonably well. To the contrary, this model system fails in the case of Ge layers, the quality of crystallinity of which is compromised because of a low growth temperature. In fact, they only show steady thermal roll-off, viz. *quenching*, without a trace of the anticipated *dequenching*.

These apparently conflicting observations can be reconciled only by considering another otherwise invisible *hidden* conduction-band valley that comes in between the L and Γ valleys to decouple them. A three-level scheme is naturally invoked thereby. Indeed, it explains not only the

missing *dequenching* but the lost local thermal equilibrium in low-quality layers. As a proof of such a conjecture, an attempt was made to directly capture the *hidden* valleys by means of time- and angle-resolved two-photon photoemission [3]. Preliminary results indicate the relevance of X(Δ)-valleys, which are slightly above the Γ -valley, in the *dequenching* of room-temperature emission as a result of ultrafast coupling of L-X(Δ)- Γ valleys by phonons taking up large crystal momenta. These are consistent with theory and luminescence study.

1. T. Sakamoto *et al.*, Appl. Phys. Lett. **105**, 042101 (2014).

2. Y. Yasutake and S. Fukatsu, Spoken at 2018 APS March Meeting (Los Angeles, 2018), P07.00012.

3. J. Kanasaki *et al.*, Phys. Rev. B **96**, 115301 (2017).

11:20am **EL+AS+EM+TF-WeM-11 Spectroscopic Ellipsometry on Organic Thin Films - From in-situ Bio-sensing to Active Layers for Organic Solar Cells**, *Eva Bittrich, P Uhlmann, K Eichhorn*, Leibniz Institute of Polymer Research Dresden, Germany; *M Schubert*, University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany; *M Levichkova, K Walzer*, Heliatek GmbH, Germany

INVITED

Nanostructured surfaces and thin films of small organic molecules, polymers or hybrid materials are promising interfaces for versatile applications like sensing, water purification, nanoelectronics, energy production and energy storage devices. Ellipsometry, as non-invasive method, is well suited to contribute to the understanding of structure – property – relationships in organic thin films, but can also act as probing technique for hybrid sensing elements. Aspects from our research ranging from switchable responsive polymer brush interfaces for biosensing to thin films of small organic molecules for organic solar cells will be presented. On the one hand, swelling of polymer brushes grafted to slanted columnar thin films of silicon will be visualized by anisotropic optical contrast microscopy, as an example for a new class of hybrid sensing materials with unique sensitivity on the nanoscale. On the other hand the effect of template molecules on the morphology and optical properties of semiconducting thin films will be discussed, emphasizing the correlation of ellipsometric data with structural analysis by grazing incidence wide angle X-ray scattering (GIWAXS).

12:00pm **EL+AS+EM+TF-WeM-13 Optical Dielectric Function of Si(bzimpy)₂ – A Hexacoordinate Silicon Pincer Complex Determined by Spectroscopic Ellipsometry**, *Yanzeng Li, M Kocherga, S Park, M Lata, M McLamb, G Boreman, T Schmedake, T Hofmann*, University of North Carolina at Charlotte

Tang and VanSlyke demonstrated light emission from the first practical electroluminescent device based on a double-organic-layer structure of tris(8-hydroxyquinoline)aluminum, Alq₃, and a diamine film in the late 80's. Since then, organic light emitting diodes (OLED) based on metal chelates such as Alq₃ have been widely studied. Despite the widespread use of Alq₃, there has been a broad search for new materials with improved properties, in particular, with respect to their chemical and electrochemical stability. We have recently reported on the successful synthesis of a neutral, hexacoordinate silicon-based fluorescent complex Si(bzimpy)₂. Our results indicate that Si(bzimpy)₂ exhibits inherent advantages such as the tunability of the luminescence in the visible spectrum, greater thermal stability, and high charge mobility that is comparable to that of Alq₃. Despite the successful synthesis and encouraging electroluminescence at 560 nm the complex dielectric function of the water stable complex has not been reported yet. Here we present spectroscopic ellipsometry data which were obtained from a Si(bzimpy)₂ thin-film in the spectral range from 300~nm to 1900~nm. A parameterized model dielectric function composed of a Tauc-Lorentz and Gaussian oscillators is employed to analyze the experimental ellipsometry data. We find a good agreement between the critical point energies observed experimentally and our density functional theory calculations reported recently.

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