Tuesday Afternoon, October 29, 2013

Manufacturing Science and Technology
Room: 202 B - Session MS+AS+EL+EM+PS+TF-TuA

Manufacturing Challenges of Nanoscale Patterning
Moderator: E.B. Svedberg, The National Academies

2:00pm **MS+AS+EL+EM+PS+TF-TuA1 Alphabet-Based Template Design Rules - A Key Enabler for a Manufacturable DSA Technology**, ***H. Yi***, *H-.S.P. Wong*, Stanford University **INVITED**

Block copolymer DSA is a result of spontaneous microphase separation of block copolymer films, forming periodic microdomains including cylinders, spheres, and lamellae. Among all the various self-assembled structures, cylinder patterns have attracted specific interest due to their great potential in patterning electrical contacts in Integrated Circuits (ICs). Due to the random distribution of electrical contacts in layouts as well as the continuous scaling of IC circuits, patterning contacts has become increasingly challenging for traditional optical lithography. Due to the advantage of low cost and sub-20 nm feature sizes, block copolymer directed self-assembly (DSA) is a promising candidate for next generation device fabrication.

Traditionally, the study of DSA has been focused on achieving long range order and a periodic pattern in large area. Chemoepitaxy approaches including using chemical patterns of preferential affinity on the substrate surface or controlling pattern formations by tuning annealing conditions have been investigated and developed. They can improve the long range order self-assembly quality and lower the defect density over large areas. In order to use DSA to pattern the randomly distributed contacts in IC layouts, we adopt physical (topographical) templates to form irregularly distributed cylindrical patterns. Topographical templates use strong physical confinements in lateral directions to alter the natural symmetry of block copolymer and guide the formation of DSA patterns. Previously we have demonstrated that for the first time the self-assembled features can be almost arbitrarily placed as required by circuit fabrication and not limited to regular patterns, by combining templates of different types on one wafer. These various templates are akin to the letters of an alphabet and these letters can be composed to form the desired contact hole patterns for circuit layouts. The capability of arbitrary placement is demonstrated in industry-relevant circuits such as static-random-access-memory (SRAM) cells and standard logic gate libraries at a dimension that is the state-of-the-art semiconductor technology today [1]. To enable introduction of DSA into manufacturing we developed a general template design strategy that relates the DSA material properties to the target technology node requirements. This design strategy is experimentally demonstrated for DSA contact hole patterning for half adders at the 14 nm and 10 nm nodes [2].

Reference:

[1] H. Yi et al. Adv. Mater, 2012.

[2] H. Yi et al. SPIE, 2013.

2:40pm **MS+AS+EL+EM+PS+TF-TuA3 Characterizing the Sensitivity of Block Copolymer Directed Self-Assembly Processes to Material and Process Variations**, ***C. Henderson***, *A. Peters, R. Lawson, P. Ludovice*, Georgia Institute of Technology

Future scaling of integrated circuits (IC) is in jeopardy due to a number of challenges related to both future material and process requirements that are needed to allow for fabrication of sub-20 nm IC devices. One of the most critical challenges is that of developing patterning technologies that can allow for formation of sub-20 nm patterned structures in a fast and economically viable manner. Due to difficulties with alternative technologies, techniques that can extend the use of current 193 nm optical lithography in a cost effective manner would be very attractive. Directed Self-Assembly (DSA) using block copolymers to perform pitch subdivision of lithographically generated primary patterns is one such promising technology. In this technique, a lithographic method is first used to define a topographic or chemical template pattern on a surface. This surface is then coated with a block copolymer that is further processes to induce microphase separation. The presence of the topographic or chemical patterns on the surface aligns, registers, and provides long range order to the formed block copolymer patterns. This microphase separation-based patterning process utilizes the propensity of the block copolymer to naturally form nanometer scale patterns whose size are dictated by the polymer block molecular weight.

The overarching goal of our work has been to develop both new block copolymers that can enable sub-20nm DSA patterning and to develop the experimental and modeling tools needed to understand the limits of such processes. In this paper, we will review our recent systematic studies of block copolymer DSA processes using state-of-the-art molecular dynamics simulations. The aim of these studies has been to identify the important material and process factors that affect the DSA process and to quantify the sensitivity of the DSA process to these factors. For example, the influence of polymer block molecular weight control and polydispersity on patterning have been rigorously quantified. Furthermore, processing factors such as guiding pattern mis-sizing and low level surface topography in the guiding pattern and their effect on DSA patterning have been studied in detail. Studies have also been performed via simulation using thermodynamic integration methods to calculate the free energy of defects in such DSA systems and the sensitivity of such defect free energies to important material and process parameters. We will review the outcomes of these studies to illustrate what the important material and process challenges will be in adapting block copolymer DSA methods into a manufacturable technology.

3:00pm **MS+AS+EL+EM+PS+TF-TuA4 DSA Patterning for sub-40 nm Pitch Features**, ***I.C. Estrada-Raygoza***, *C. Liu, Y. Yin, J. Abdallah,* IBM Albany Nanotech Center*, S. Mignot,* GLOBALFOUNDRIES U.S. Inc.*, B.G. Morris, M.E. Colburn,* IBM Albany Nanotech Center*, V. Rastogi, N. Mohanti, A. Raley, A. Ko*, TEL Technology Center, America, LLC

As the semiconductor industry targets sub-40 nm pitch features, there will be a necessity for new patterning techniques which allow for the extension beyond single ArF-immersion patterning capability of 38 half pitch features. To meet today's aggressive design requirements, double patterning techniques, such as Pitch Splitting (PS) Lithography and Sidewall Image Transfer (SIT), have been widely used. Below 38 nm pitch design the industry has looked toward Extreme Ultraviolet (EUV), Double Sidewall Image Transfer (SIT2) and Directed Self-Assembly (DSA) as strong emerging candidates. A major component to the success of the DSA technique is the development of effective etch processes. This talk targets to discuss the challenges and innovations of the plasma etch process on sub-40 nm pitch features produced by DSA chemo and grapho-epitaxy guiding patterns. Each DSA scheme presents different challenges, depending of the aspect ratio, density of the patterns and etch stack materials, but in general, the parameters that have been studied are selectivity to both masking and etched materials, across wafer profile uniformity, critical dimension (CD) uniformity and line-edge/line-width roughness (LER/LWR). This work was performed by the Research Alliance Teams at Albany IBM Research and Development Facilities.

4:40pm **MS+AS+EL+EM+PS+TF-TuA9 Advanced Gate Patterning Techniques for 14nm Node and Beyond**, ***F.L. Lie***, *R. Jung, Y. Yin, A. Banik, S. Kanakasabapathy, J.C. Arnold, S. Seo, B. Haran,* IBM Corporation*, Y. Moon, L. Jang, S. Bentley,* GLOBALFOUNDRIES U.S. Inc.*, H. Kang, D. Bae,* Samsung Electronics Co.*, A. Metz, C. Cole, K. Ito, S. Voronin, A. Ko, A. Ranjan, K. Kumar*, TEL Technology Center, America, LLC

For advanced CMOS nodes, traditional patterning processes are challenged to meet the technology needs of certain key levels. For example, conventional 193nm immersion lithography is not able to resolve features below 40nm half pitch with a single exposure without severe design rule restrictions. Until further wavelength scaling through Extreme Ultraviolet (EUV) has matured, the industry's attention is focused on advanced patterning schemes such as Pitch Splitting (PS) Lithography and Sidewall Image Transfer (SIT). In PS, a pattern is defined by two lithography exposure with a certain coordinate shift between the two exposures. PS can be achieved through either litho-etch-litho-etch or litho-litho-etch. In SIT, a pattern is defined by creating a mandrel in one lithography exposure, depositing a conformal spacer film on the mandrel, and pulling out the mandrel, resulting in two standing spacer for the pattern frequency doubling. This work evaluated the advantages and technical challenges of PS and SIT patterning schemes for line-space application. We will focus on CD uniformity improvement, line edge/line width roughness control, pitch walk control, and the extendability of each technique. RIE challenges common to double patterning such as through pitch etch bias will also be discussed.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities and in joint development with TEL Technology Center, America, LLC

5:00pm **MS+AS+EL+EM+PS+TF-TuA10 High Throughput Electrospinning of Ceramic Nanofibers**, ***S. Sood***, *P. Gouma*, State University of New York at Stony Brook (Stony Brook University)

High yield nanomanufacturing has been the focus of greater attention due to the emerging importance of functional nanomaterials. Electrospinning is a

nanomanufacturing process that faces challenges as far as its scalability is concerned. Even the existing high-throughput electrospinning systems are limited to processing thin layers of polymer nanofibrous mats. Nanofibrous ceramics have rarely been studied with respect to their electrospinning processing. On the other hand, electrospun nanowires of ceramics are key to nanotechnology and nanomedicine applications (e.g. electrospun MoO_3 nanowires have been used as ammonia sensors for application in non-invasive diagnostics [1]). In this study, the scalable synthesis of ceramic oxide nanomats by the multi-jet design that we developed and built and which enables very high yield of ceramic nanofibers is discussed. As a scaled up approach to traditional needle electrospinning [2], up to 24 jets are spun simultaneously using similar processing parameters as a traditional needle set up. Due to a thin metallic disc design, with tiny holes drilled at the disc, the electric field is evenly distributed to all jets. Continuous replenishment of the source disk at higher flow rates allows for high yields of nanofibers.

P. Gouma, K. Kalyanasundaram, and A. Bishop, "Electrospun Single Crystal MoO3 Nanowires for Bio-Chem sensing probes", Journal of Materials Research, Nanowires and Nanotubes special issue, 21(11), pp. 2904-2910, 2006.

S. Sood, S. Divya, P. Gouma, “High throughput electrospinning of 3D nano fibrous mats”. Journal of Nanoengineering and Nanomanufacturing. Accepted Publicaition. In Print, 2013.

5:20pm **MS+AS+EL+EM+PS+TF-TuA11 Manufacture and Characterization of Silver and Copper Nanorods Produced via Forcespun Nylon 6 Nanofibers Templates**, ***D.M. Mihut***, *K. Lozano, W. Zhao*, The University of Texas Pan American

The Nylon 6 nanofibers are produced using the forcespinning method and further on coated with metallic thin films using the thermal evaporation equipment. The Nylon 6 nanofibers are used as templates in order to obtain silver and copper nanorods where the polymer is removed after high temperature calcination from the metallic coated structures. The metallic nanorods morphology and electrical behavior are characterized using the scanning electron microscopy, scanning transmission electron microscopy (SEM, STEM), energy disperssive X-ray spectroscopy (EDX) and electrical measurements. This method of fabrication offers the ability to obtain controlled ultrafine size netallic nanorods.

Spectroscopic Ellipsometry Focus Topic
Room: 101 A - Session EL+AS+EM+SS+TF-WeA

Spectroscopic Ellipsometry: Perspectives and Novel Applications

Moderator: T. Hofmann, University of Nebraska-Lincoln, S. Zollner, New Mexico State University

2:00pm **EL+AS+EM+SS+TF-WeA1 Optical Hall Effect - Detection of Symmetric and Anti-Symmetric Landau-Level Transitions in Multilayer Epitaxial Graphene on C-face SiC**, ***P. Kühne****, Univ. of Nebraska-Lincoln, *V. Darakchieva,* Linköping Univ., Sweden, *J.L. Tedesco,* ABB, Inc, *R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill,* U.S. Naval Research Lab, *C.M. Herzinger,* J.A. Woollam Co., Inc., *M. Schubert, T. Hofmann*, Univ. of Nebraska-Lincoln

We report on polarization sensitive, magneto-optic, reflection-type Landau level (LL) spectroscopy at low temperatures by using the optical-Hall effect in the mid-infrared spectral range (from 600 to 4000 cm^{-1}) on epitaxial graphene grown on C-face silicon carbide by thermal decomposition. In contrast to transmission measurements, our reflection-type ellipsometry setup allows simultaneous detection of Landau level transitions, and the classical Drude-type magneto-optic free charge carrier contribution throughout the full mid-infrared spectral range, including the opaque Reststrahlen band of the SiC substrate. In this region, we observe a multitude of LL transitions that can be assigned to single-, bi- and Bernal stacked (ABA) tri-layer graphene.[12] For the first time, we observe symmetric and anti-symmetric signatures due to non-polarizing, i.e., isotropic, and polarizing, i.e., anisotropic Landau level transitions, respectively. Isotropic polarization behavior is found for LL transitions exhibiting a square-root dependence on the magnetic field, typical for stacks of decoupled graphene mono-layers. Anisotropic polarization behavior is observed for LL transitions with a sub-linear to linear dependence on the magnetic field, indicative for bi- and ABA stacked tri-layer graphene. We present a dielectric model describing contributions from the substrate, Drude-type free charge carrier and symmetric and non-symmetric Landau level transitions. Model parameters as the average velocity of Dirac fermions c = (1.01±0.01) 10^6 m/s and interlayer coupling constant γ = (3150±50) $cm^{-1}$are found to been in excellent agreement with previously reported values.

[1] M. Koshino and T. Ando, Phys. Rev. B **77**, 115313 (2008).

[2] M. Orlita, C. Faugeras, R. Grill, C. Berger, W. A. de Heer, G. Martinez, M. Potemski, et al., Phys. Rev. Lett. 107, 216603 (2011).

2:20pm **EL+AS+EM+SS+TF-WeA2 A Physical Model Dielectric Function for Graphene from the THz to the UV**, ***A. Boosalis****, University of Nebraska-Lincoln, *W. Li, R. Elmquist, M. Real, N.V. Nguyen,* National Institute of Standards and Technology (NIST), *M. Schubert,* University of Nebraska-Lincoln, *R. Yakimova, V. Darakchieva,* Linköping University, Sweden, *R.L. Myers-Ward, C. Eddy, D.K. Gaskill,* Naval Research Laboratory, *T. Hofmann*, University of Nebraska-Lincoln

Graphene has been the focus of much recent research due to its unique electronic and optical properties, with potential for high performance electronics, tunable ultra-fast lasers, and transparent electrodes. Further development of graphene requires a complete understanding of graphene's optical properties. Once thought to be trivially related to the lattice constant, it has become clear that graphene's dielectric response contains distinct absorption features at ~4.5 and ~6 eV. However, the scientific community currently lacks consensus as to the origin of each feature [1,2].

In order to determine the physical origin of both absorption features, we have carried out spectroscopic ellipsometry measurements from 0.75 to 9 eV on graphene grown by CVD on Cu and by high-temperature Si sublimation from SiC. CVD grown graphene was transplanted to a fused silica substrate prior to measurement, while measurements conducted on SiC included 3C and 6H SiC polymorphs, before and after hydrogen intercalation.

Experimental data were analyzed with a biaxial model dielectric function which is dependent on the graphene joint density of states and modified by the Fano configuration interaction to account for exciton absorption [3]. Physical parameters include the electron next-neighbor hopping energy, the exciton resonant energy, the exciton absorption affinity, and the graphene optical thickness. All parameters are varied until the lowest mean squared error between model dielectric function and experimental spectra is achieved.

Our results show that the absorption ~4.5 eV is excitonic, while the absorption ~6 eV is an interband transition arising from the saddle point at the M position in the graphene band structure, a similar result to optical properties predicted by density functional theory [4]. The strain in the graphene lattice can be estimated from the next-neighbor hopping energy, and our results demonstrate relaxation in the graphene lattice after hydrogen intercalation of graphene on SiC. Epitaxial graphene on SiC also shows a higher affinity for exciton production and a lower exciton binding energy than graphene grown by CVD.

References:

[1] Mak et al., Phys. Rev. B. 106, 046401 (2011)

[2] Santoso et al., Phys. Rev. B. 84, 081403 (2011)

[3] Chae et al., Nano. Lett. 11, 1379 (2011)

[4] Yang et al., Phys. Rev. Lett. 103, 186802 (2009)

2:40pm **EL+AS+EM+SS+TF-WeA3 Spectroscopic Ellipsometry – A Perspective**, ***D.E. Aspnes***, North Carolina State University **INVITED**

Since its initial development in the early 1970's, spectroscopic ellipsometry (SE) has become the primary technique for determining optical properties of materials. In addition to the other historic role of ellipsometry, determining film thicknesses, SE is now widely used to obtain intrinsic and structural properties of homogeneous and inhomogeneous materials in bulk and thin-film form, including properties of surfaces and interfaces. Its nondestructive capability for determining critical dimensions has made SE indispensible in integrated-circuits technology. The presentation is directed toward those who are unfamiliar with SE but may feel that it could provide useful information in specific situations. Accordingly, I give some background and basic theory, then illustrate capabilities with a variety of applications. Probable directions for the future are also discussed.

4:00pm **EL+AS+EM+SS+TF-WeA7 The First Report of MetA-SIMS with Bismuth Over Layers**, *M.R. Linford,* ***N. Madaan***, Brigham Young University

The low ionization yields of many sputtered moieties is a bottleneck for completely exploiting the tremendous potential of ToF-SIMS. Among the many procedures for improving ionization efficiencies in SIMS, a significant amount of work has been directed towards metal assisted SIMS (MetA-SIMS). In this procedure a thin film (ca. 2 nm) of a metal (Au or Ag) is deposited on a sample surface before SIMS analysis. The resulting secondary ion yields have been shown to increase substantially for many polymers, where the yield enhancement is found to be fragment specific and also to depend on the type of primary ion and sample used. In our work we are studying MetA-SIMS on spin coated polyethylene glycol surfaces using thin layers of bismuth. To be best of our knowledge, MetA-SIMS with Bi over layers has not previously been reported. In particular, we are striving to incorporate spectroscopic ellipsometry (SE) as a tool to accurately find the thickness of deposited metal so that we can best understand the correlation between Bi film thickness and ionization yield enhancements. When a QCM crystal is used to monitor the thickness of a film of a deposited metal on a sample surface, one assumes that the sticking coefficient of the evaporated metal is the same for both the QCM crystal and the sample surface. However, it has now been shown that the sticking coefficient on a polymer surface can be $1/10^{th}$ of that on the QCM crystal. Thus a different film measurement technique is needed to more accurately allow us to determine the thicknesses of metal films on polymer surfaces. To best determine our Bi thicknesses by SE (from ca. 200 – 1000 nm) we have used the interference enhancement technique – a ca. 500 nm oxide on silicon substrate. Of course SE is also a very fast and non-invasive technique for film thickness determination compared to AFM or XPS. Unlike Au, Bi and Ag appear to form a thin oxide layer that may chemically affect the SIMS ionization process. Accordingly, we compare the MetA-SIMS of polyethylene glycol films using Au, Bi, and Ag with all thicknesses determined by SE. XPS is used in parallel to determine the amount of oxide on the metals and to confirm their deposition.

*** Spectroscopic Ellipsometry Graduate Student Award Finalist**

4:20pm **EL+AS+EM+SS+TF-WeA8 Spectroscopic Ellipsometry of Thin Films for Archival Optical Data Storage and for Microfabricated Thin Layer Chromatography Plates**, ***M.R. Linford***, *A. Diwan, S. Kanyal, H. Wang, N. Madaan,* Brigham Young University*, A. Dadson,* Diamond Analytics*, R.C. Davis, B. Lunt,* Brigham Young University*, N. Podraza*, The University of Toledo

Our group is focused on the synthesis and characterization of new materials and over the years this interest has led us into different research areas. Of late we have focused on developing and understanding the materials for archival optical data storage and for separations science (chromatography). In particular, we have recently helped spin out a company from the university that is selling a DVD that has been shown to last for more than 1000 years – see www.mdisc.com. Another company has licensed our technology to microfabricate thin layer chromatography (TLC) plates – see www.diamond-analytics.com.

In this talk we discuss the important role that spectroscopic ellipsometry (200 – 1000 nm) has played in the development and understanding of the materials in these devices. For many of these measurements we use interference enhancement to break the correlation between film optical constants and thicknesses. Some of our measurements have been fairly routine. For example, the thicknesses and optical properties of the ca. 35 nm alumina barrier layers in our microfabrication of TLC plates are easily modeled using a Cauchy dispersion relationship. In other cases the analyses have been challenging, e.g., the thin, ca. 6 nm, Fe films used to make TLC plates appear to be completely oxidized, but thicker Fe films show increasing metallic (Drude) character. An understanding of the optical properties of our bismuth-tellurium-selenium (BTS) write layers on Mylar tape for optical data storage has also been nontrivial. These films show high levels of roughness by AFM, significant void fractions by RBS, and moderately high levels of oxidation by XPS and SIMS, which mandated the use of a roughness layer and optimization of the depolarization factor in the effective medium approximation that described the film. AFM and SEM were also used to characterize these materials, and our final SE analysis of this material might not have been reasonable without the extra information these techniques provided. Both the BTS write layer and Fe films for TLC have been monitored over an extended period of time by SE. The resulting plots of psi and delta vs. several wavelengths reveal the long-term stabilities of these materials. At present we are also attempting to determine the optical constants of the carbon nanotube forests used as templates in TLC plate microfabrication. We believe that the resulting optical constants of these materials, which should show a considerable degree of anisotropy, will be of interest to the community.

4:40pm **EL+AS+EM+SS+TF-WeA9 Optical Properties of Nanoscale Nanoelectronic Materials**, ***A.C. Diebold***, College of Nanoscale Science and Engineering **INVITED**

Nanoscale dimensions clearly alter the optical properties of materials. All too often, changes in key optical properties such as direct gap transitions are attributed to quantum confinement. The origin of changes in optical properties depends on several factors including crystal structure (poly-crystalline vs single crystal), material type (metal, semiconductor, or dielectric) and temperature. Temperature dependent determination of the dielectric function of ultra-thin silicon on insulator films show that electron-phonon interactions alter optical transitions. Thus changes in the phonon dispersion will alter room temperature optical properties. These changes can be due the films that surround the nanolayer. Other examples include silicon fins and silicon fins topped with Si(1-x)Gex layers. The Si fins are confined in two dimensions. Here the need for understanding anisotropic optical properties is described. The optical properties of metal films also show dimensional effects. The origin of the thickness dependence of the optical properties of poly-crystalline metal films can be traced to grain size. In this talk, the impact of nanoscale dimensions will be explored using examples that include ultra-thin silicon films, thin silicon "fin" structures, and poly-crystalline thin metal films.

5:20pm **EL+AS+EM+SS+TF-WeA11 Optical Constants of $Ni_{1-x}Pt_x$ Silicides from Spectroscopic Ellipsometry**, ***L.S. Abdallah****, *S. Zollner,* New Mexico State University*, C. Lavoie, A. Ozcan,* IBM*, M. Raymond*, GLOBALFOUNDRIES

Nickel silicides are widely used in semiconductor manufacturing as contacts in CMOS device processing to achieve highly stable low-resistance contacts between copper back-end metallization and front-end silicon transistors. We provide a comprehensive analysis of the dielectric function and optical conductivity for nickel platinum silicides with different platinum concentrations (0 to 30 at.% Pt). Our goal is in-line process control of Ni-Pt alloy deposition and silicide formation using spectroscopic ellipsometry.

Previously, we determined the optical constants of $Ni_{1-x}Pt_x$ metal alloys. We deposited 100 Å $Ni_{1-x}Pt_x$ alloy films with different Pt compositions (0 to 25 at.% Pt) on a thick layer of SiO_2 to prevent the reaction between the metal and the silicon. Ellipsometric measurements were performed on these samples from 0.6 to 6.6 eV using a broad range of angles of incidence (20 to 80°). Using a thick transparent layer of SiO_2 as well as using a broad range of angles of incidence, we vary the optical path length and thus obtain more information about our metal films.

After determining accurate optical constants of $Ni_{1-x}Pt_x$, alloys with the same thickness were deposited directly on Si to study the optical constants of silicides. Ellipsometric measurements were performed over the same photon energy range (0.6 to 6.6 eV), but using a smaller range of incident angles because of the absence of SiO_2 underneath the metal (no sharp interference fringes).

During $Ni_{1-x}Pt_x$ deposition on Si, some metal atoms will diffuse into the Si substrate even at room temperature, creating a metal-rich silicide. Annealing the samples at 500˚ C for 30 s creates a monosilicide layer with a thickness of about 200 Å . No unreacted metal remains. We include a 10 Å layer of SiO_2 as a native oxide in our model. To obtain the correct silicide thickness, we tried different thicknesses (all around 200 Å) and then we picked the thickness that eliminates Si substrate artifacts.

The imaginary part of the resulting dielectric function of monosilicides shows metallic Drude behavior with two additional peaks at 1.5 eV and 4.5 eV due to interband electronic transitions. Our results will be compared to previous measurements and electronic structure calculations on NiSi and PtSi. In our results, absorption peaks broaden with increasing Pt content in the silicides, similar to our earlier results for $Ni_{1-x}Pt_x$ metal alloys.

5:40pm **EL+AS+EM+SS+TF-WeA12 Anisoptropic Bruggeman Effective Medium Approaches for Slanted Columnar Thin Films**, ***D. Schmidt***, *E. Schubert, M. Schubert*, University of Nebraska-Lincoln

Two different formalisms for the homogenization of composite materials containing ellipsoidal inclusions basedon Bruggeman's original formula for spherical inclusions can be found in the literature [1,2]. Both approximations to determine the effective macroscopic permittivity of such an idealized composite assume randomly distributed dielectric particles of equal shape and differ only in the definition of the depolarization factors. The two approaches are applied to analyze ellipsometric Mueller matrix spectra acquired in the visible and nearinfrared spectral region from metal and semiconductor slanted columnar thin films. Furthermore, the effective dielectric function tensor generated by the two Bruggeman formalisms is compared to effective major axes dielectric functions individually determined with an assumption-free homogeneous biaxial layer approach.

Best-match model parameters of all three model approaches are discussed and compared to estimates fromscanning electron microscope images. It was found that all three optical model equivalents for slanted columnar thin films agree well with the imaging technique and that no preference can be given to any one of the two Bruggeman formalism in terms of structural properties determination.

Application of the effective medium approximation models will be highlighted on the example of in-situ monitoring of dielectric and metal conformal coating growth onto slanted columnar thin films by atomic layer deposition.

[1] D. Polder and J. H. van Santen, Physica 12, 257 (1946).

[2] Mackay and Lakhtakia, J. Nanophoton. 6, 069501 (2012).

*** TFD James Harper Award Finalist**

Spectroscopic Ellipsometry Focus Topic
Room: 101 A - Session EL+AS+EN+PS+SS+TF-ThM

Spectroscopic Ellipsometry for Photovoltaics and Instrument Development

Moderator: M. Creatore, Eindhoven University of Technology, Netherlands

8:00am **EL+AS+EN+PS+SS+TF-ThM1 Application of Spectroscopic Ellipsometry for the Characterization of Various Solar Cell Devices**, ***H. Fujiwara***, Gifu University, Japan **INVITED**

To establish new structural characterization methods for Si-based and $CuInGaSe_2$(CIGS)-based solar cells, we have developed spectroscopic ellipsometry (SE) techniques that can be applied for the analysis of various textured structures used in the solar cell devices. In particular, our SE analyses allow the structural characterization of (i) hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) tandem-type solar cells, and (ii) a-Si:H/crystalline Si (c-Si) heterojunction solar cells, both fabricated on textured substrates. For the determination of a-Si:H and μc-Si:H properties, optical databases in which the optical constants of a-Si:H and μc-Si:H are described by micro-structural factors have been constructed.[1,2] Furthermore, by developing a new optical model, we have confirmed that the high-precision analysis of a-Si:H/μc-Si:H multilayer stacks can be performed even on textured substrates having sub-micron size rough surface. On the other hand, to determine the thickness and properties of a-Si:H layers incorporated into textured a-Si:H/c-Si solar cells, SE with a tilt angle measurement configuration[3,4] has been employed. In this technique, samples are tilted so that the specular light reflection on the texture facets is measured. From this technique, we have succeeded in characterizing the properties of quite thin a-Si:H layers (5 nm) on the c-Si textures. Recently, we have applied the SE technique further to establish the structural characterization method for CIGS-based solar cells.[5] For the SE analysis, we have constructed an optical database in which the CIGS dielectric function can be calculated as functions of the Ga composition x=Ga/(In+Ga) and Cu composition y=Cu/(In+Ga). By using the constructed optical database, we have demonstrated that the structure and compositions of CIGS-based thin films can be determined accurately.

1) Kageyama et al., Phys. Rev. B 83, 195205 (2011), 2) Yuguchi et al., J. Appl. Phys. 111, 083509 (2012), 3) Saenger et al., Thin Solid Films 518, 1830 (2010), 4) Watanabe et al., Appl. Phys. Express 3, 116604 (2010), 5) Minoura et al. J. Appl. Phys. 113, 063505 (2013).

9:00am **EL+AS+EN+PS+SS+TF-ThM4 Real-Time and Through-the-Glass Mapping Spectroscopic Ellipsometry for Analysis of CdS/CdTe Coated Superstrates and Correlations with Solar Cell Performance**, ***P. Koirala***, *J. Chen, X. Tan, R.W. Collins*, The University of Toledo

In-situ real-time spectroscopic ellipsometry (RT-SE) from the film side has been applied along with ex-situ spectroscopic ellipsometry through the glass (TG-SE) toward the analysis of the different stages of CdS/CdTe solar cell fabrication in the superstrate configuration. The RT-SE studies of the CdS and CdTe layers deposited on transparent conducting oxide (TCO) coated glass superstrates provide information on the CdS growth, its surface roughness evolution, as well as overlying CdTe interface formation and bulk layer growth. Such information is very useful for developing a realistic optical model for the as-deposited layer structure in TG-SE mapping analysis over the full 15 cm x 15 cm superstrate area. In the mapping analysis, a mask is used to measure all 256 points where 0.125 cm^2 area dot cells are to be made. Because the as-deposited superstrate/film-structure undergoes additional processing steps, however, in order to complete the solar cell devices, three sets of TG-SE data maps are collected that characterize the superstrate/film-structure in the (i) as-deposited, (ii) $CdCl_2$-treated, and (iii) back-contact patterned states. With the optical database that has been established for both the as-deposited and $CdCl_2$ treated CdS and CdTe, each of the three TG-SE data maps has been analyzed based on an optical model deduced from RT-SE studies of the CdS and CdTe depositions. By using these SE techniques, we have been able to quantify the spatial dependence of the changes that occur in the superstrate/film-structure as a result of the different processing steps. In order to corroborate the layer structure determined by TG-SE, comparisons with cross-sectional transmission electron microscopy (XTEM) have been performed for selected states of the superstrate/film-structure and for selected locations. The results have been found to validate the overall RT-SE and TG-SE approach and analysis results. Finally, the layer parameters as determined from the TG-SE analyses have been correlated statistically with the device performance of the 256 dot cells fabricated over the final 15 cm x 15 cm superstrate/film-structure. The resulting correlations expedite solar cell optimization.

9:20am **EL+AS+EN+PS+SS+TF-ThM5 Expanded Beam Spectroscopic Ellipsometry for In-line Monitoring of Thin Film Process**, ***M. Fried***, Hungarian Academy of Science, Hungary **INVITED**

Non-destructive analysing tools are needed at all stages of thin film process-development, especially photovoltaic (PV) development, and on production lines. In the case of thin films, layer thicknesses, micro-structure, composition, layer optical properties, and their uniformity are important parameters. An important focus is to express the dielectric functions of each component material in terms of a handful of wavelength independent parameters whose variation can cover all process variants of that material. With the resulting database, spectroscopic ellipsometry coupled with multilayer analysis can be developed for on-line point-by-point mapping and on-line line-by-line imaging.

This talk will try to review the investigations of different types of PV-layers (anti-reflective coating, transparent-conductive oxide (TCO), multi-diode-structure, absorber and window layers, backreflector) showing the existing dielectric function databases for the thin film components of CdTe, CIGS, thin Si, and TCO layers.

Off-line point-by-point mapping can be effective for characterization of non-uniformities in full scale PV panels in developing labs but it is slow in the on-line mode when only 15 points can be obtained (within 1 min) as a 120 cm long panel moves by the mapping station. Last years [1, 2], a new instrumentation was developed that provides a line image of spectroscopic ellipsometry (wl=350-1000 nm) data. Upto now a single 30 point line image can be collected in 10 s over a 15 cm width of PV material [3, 4]. This year we are building a 30 and a 60 cm width expanded beam ellipsometer which speed will be increased by 10 X. Then 1800 points could be mapped in a 1 min traverse of a 60*120 cm PV panel or flexible roll-to-roll substrate. Another enhancement is the switch-over to rotating compensator measuring principle.

[This work was supported by the ENIAC E450EDL and KMR_12_1_2012_0225 projects]

[1] C. Major, G. Juhasz, Z. Horvath, O. Polgar, M. Fried, *PSS (c)*, **5**, 5 (2008).

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[3] M. Fried, G. Juhász, C. Major, P. Petrik, O. Polgár, Z. Horváth, A. Nutsch, *Thin Solid Films***519**, 2730 (2011).

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10:40am **EL+AS+EN+PS+SS+TF-ThM9 Materials Characterization using THz Ellipsometry and THz Optical Hall Effect**, ***T. Hofmann***, University of Nebraska-Lincoln **INVITED**

Ellipsometry in the THz spectral range has been demonstrated to be a very versatile tool for the investigation of semiconductor heterostructures, meta-materials, 2D electron gases (2DEG), and even graphene.

In this talk, instrument development with particular emphasis on frequency-domain, rotating optical element THz ellipsometry will be reviewed and recent progress on THz optical Hall-effect systems, which encompasses generalized ellipsometry in magnetic fields, will be discussed.

The application of THz ellipsometry for the accurate measurement of complex optical constants of isotropic and anisotropic bulk materials and thin films will be illustrated briefly. The progress on THz generalized ellipsometry investigations of 3D metal nanostructured thin films will be reported in detail. The investigated films exhibit a strong anisotropic optical response in the THz spectral range. It will be demonstrated that the anisotropic optical response of 3D nanostructures changes drastically as the function of the dielectric properties of the ambient. Applications for 3D metal nanostructured thin films as THz optical sensors will be discussed.

In addition, recent results on application of THz optical Hall-effect measurements will be reported. Exemplarily, temperature-dependent THz optical Hall-effect investigations of AlGaN/GaN high electron mobility transistors structures are shown. Our findings indicate that the 2DEG sheet density is independent of the sample temperature. The mobility and effective mass, however, strongly depend on the sample temperature. The mobility shows a strong increase with decreasing temperature largely due to the reduction of LO phonon scattering. The opposite behavior is observed for the effective mass and explained by the reduction of the 2DEG

confinement, i.e., the wave function penetration of the AlGaN with increasing temperature.

11:20am **EL+AS+EN+PS+SS+TF-ThM11 A History of Early Ellipsometry and Polarimetry**, ***R.A. Synowicki***, J.A. Woollam Co., Inc.

This work surveys the early history of polarimetry and ellipsometry. Special consideration is given to the time period between Drude's original work in the late 1880's and the work of Rothen in the mid 1940's.

Snell determined the refractive index of water in 1621. Isaac Newton followed in the 1660's with the prism minimum deviation technique. In the late 1880's August Kundt measured the optical properties of very thin metal films by minimum deviation, but a better technique was needed for absorbing materials.

The polarimeter was invented around 1840. Early polarimetry was used to measure the rotation of polarized light through solutions of sugar, and used in customs offices at seaports for taxation of sugar shipments. In 1845 the Faraday effect showed rotation of polarization by a magnetic field, a result later explained by James Clerk Maxwell's electromagnetic theory.

Paul Drude applied Maxwell's theory to describe the internal structure of materials. To experimentally determine optical properties Drude developed ellipsometry as an analytical technique between 1885 and 1890. Null ellipsometry techniques were originally used, but in the following decades half-shade techniques with improved accuracy became common.

Ellipsometry remained a popular technique after the time of Drude. A surprising amount of this early ellipsometry work was spectroscopic. By 1910 R.S. Minor, A.Q. Tool, and L.R. Ingersoll used ellipsometry to determine the optical constants of metals over a wide spectral range from 226 nm in the ultraviolet to 2250 nm in the infrared.

11:40am **EL+AS+EN+PS+SS+TF-ThM12 Vibrational Properties of Lanthanum Aluminate and Magnesium Aluminate Spinel Using Fourier Transform Infrared Ellipsometry**, ***T. Willett-Gies***, New Mexico State University, *C.J. Zollner,* Cornell University, *E. DeLong, S. Zollner*, New Mexico State University

Using FTIR ellipsometry, we have determined the dielectric function of twinned single-crystalline lanthanum aluminate ($LaAlO_3$) and spinel ($MgAl_2O_4$) wafers which are often used as substrate materials for oxide epitaxy. Measurements were taken at 300 K in the region of lattice vibrations between 250 and 1000 cm^{-1}. $LaAlO_3$ is a rhombohedrally distorted perovskite with two formula units per unit cell, leading to eight IR-active phonon modes [1]. Two of these eight are below our spectral range, one is very weak, and two are nearly degenerate [1]. We thus expect four TO peaks in the imaginary part of the dielectric function. The polar character of $LaAlO_3$ also causes strong LO-TO splittings. Unlike previously published FTIR reflectance studies (which require a Kramers-Kronig analysis to determine the TO/LO phonon peaks), our FTIR ellipsometry measurements allow the direct determination of TO and LO phonon energies as peaks in the dielectric function ε and the loss function 1/ε, respectively.

Magnesium aluminate spinel ($MgAl_2O_4$) belongs to the cubic O_h^7 space group and has two formula units per primitive cell. Of its 39 optic modes, factor group analysis [2] shows that there are only four IR-active modes with T_{1u} symmetry. The lattice dynamics of spinel has long been controversial and differences have been found between natural crystals (which are believed to be fully ordered) and synthetic crystals (which often contain a small amount of Mg/Al disorder).

A good description of the dielectric functions of these materials can be found using a sum of Lorentz oscillators (for the TO phonons in our spectral range) and two poles for electronic and low-energy phonon absorption outside of our spectral range. A factorized model [3] with LO/TO phonon pairs and a UV pole yields even better agreement with the data. The classical Lorentz model assumes a frictional force proportional to the velocity of the atoms resulting in a single broadening parameter, while the Lowndes model [3] takes into account the anharmonic phonon decay and assigns independent broadening parameters to the LO and TO phonons. Our FTIR ellipsometry measurements yield LO and TO parameters (energies, broadenings, and oscillator strengths) with unprecedented accuracy, far exceeding those from previous FTIR reflectance results. We will compare our experimental phonon energies with those obtained from *ab initio* density-functional theory for both $LaAlO_3$ and $MgAl_2O_4$.

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

Spectroscopic Ellipsometry Poster Session

EL-ThP2 Electronic and Vibrational Properties of Nickel Oxide using Spectroscopic Ellipsometry, ***C.M. Nelson***, *T. Willett-Gies, L.S. Abdallah, S. Zollner*, New Mexico State University

Nickel oxide (NiO) is an interesting material, because it is a Mott-Hubbard charge-transfer insulator and also displays antiferromagnetic ordering of electron spins [1]. Spectroscopic ellipsometry is able to investigate the electronic structure of NiO (from the visible and UV portions of the spectra) and also its lattice dynamics (using infrared ellipsometry). Our interest in the NiO optical constants is also of a practical nature, to model ellipsometry spectra of bulk Ni and Ni thin films with a native oxide of NiO.

We measured the ellipsometric angles ψ and Δ for single-side polished bulk NiO from 0.8 to 6.5 eV with angles of incidence from 65 to 75° to determine the dielectric function. A dispersion model for the optical constants was built using two Tauc Lorentz oscillators; one with a Lorentz oscillator resonance energy at 3.96 eV and a second one with a much smaller amplitude at 6.40 eV. These peaks are in agreement with reflectance data analyzed using Kramers-Kronig transforms [2]. Our model also included a surface roughness layer with 40 Å thickness. Atomic force microscopy measurements confirmed this layer, showing an RMS roughness of 42.5 Å. We will report accurate dielectric function data for NiO from 0.8 to 6.5 eV.

FTIR ellipsometry was also performed on bulk NiO from 290 to 1000 cm^{-1} to study the lattice vibrations. TO phonons were found at 392 cm^{-1} and 551 cm^{-1}, with the corresponding LO modes at 592 cm^{-1} and 545 cm^{-1}. The weak TO mode at 551 cm^{-1} results from the antiferromagnetic ordering of NiO, which doubles the unit cell and causes zone folding, making a zone-edge TO mode infrared-active. Previous FTIR absorption measurements of NiO [3] did not report the infrared-active zone-edge phonon. Usually, antiferromagnetic ordering is only observed using neutron scattering, not with FTIR optical methods.

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EL-ThP3 Properties of Sm Doped CeO_2 Thin Films Prepared by Liquid Solution Deposition, *K.N. Mitchell, C.A. Rodriguez, T. Willett-Gies, Y. Li,* ***S. Zollner***, New Mexico State University

Cerium(IV) oxide, also known as CeO_2 or ceria, is a transparent (insulating) oxide of the rare earth metal cerium. It is an ionic conductor with applications in fuel cells, as a catalyst, or for photovoltaic water splitting (hydrogen production). Thin films of ceria produced by RF magnetron sputtering on sapphire at 770C have been studied extensively by Arwin's group (S. Guo et al., J. Appl. Phys. 77, 5369, 1995). They found changes in grain size, surface morphology (visible in AFM images), and optical constants varying with the film thickness. By contrast, we report analysis results for relatively thick (300-500 nm) ceria films prepared by liquid solution deposition (dip-coating) followed by annealing. We also investigate the effect of samarium doping (up to 20at.%) of ceria. The rare earth metal samarium usually forms a sesquioxide Sm_2O_3. Therefore, doping ceria with Sm is expected to lead to the formation of oxygen vacancies, which enhances the ionic conductivity of ceria. Our ellipsometry spectra (ellipsometric angles and depolarization) can be described very well in the transparent region (below 3 eV) using a Tauc-Lorentz dispersion model for ceria, if small amounts of surface roughness and thickness non-uniformity across the wafer are taken into account. Once these thickness parameters have been determined for our films, we obtain the optical constants of CeO_2:Sm using a basis spline expansion. We find the typical dispersion expected for an insulator with a direct band gap near 3.7 eV. Samarium doping causes a significant decrease of the refractive index in the transparent region. Most likely, the films with high Sm content are less dense (have more voids, perhaps due a smaller crystallite size) than pure ceria films. An increase in disorder due to Sm doping was also found in x-ray diffraction studies of electrodeposited ceria films (Phok and Bhattacharya, phys. status solidi (a) 203, 3734, 2006). As expected from Kramers-Kronig consistency, we find a significant reduction of the height of the main absorption peak at 4 eV. The direct band gap, however, remains at 3.7 eV, independent of Sm content. There is, however, a significant decrease in the slope of the onset of absorption with increasing Sm content. In addition to ellipsometry results, we will also report AFM, XRD, Raman, and (perhaps) FTIR ellipsometry results for our Sm-doped ceria films.

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