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**

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