## Spectroscopic Ellipsometry Focus Topic
## Room 304 - Session EL+AS+EM-TuM

### Optical Characterization of Thin Films and Nanostructures

**Moderators: Tino Hofmann**, University of North Carolina at Charlotte, **Mathias Schubert**, University of Nebraska - Lincoln

8:00am **EL+AS+EM-TuM-1 Femtosecond Time Resolved Pump-Probe Spectroscopic Ellipsometry – Applications and Challenges**, ***Rüdiger Schmidt-Grund,*** TU Ilmenau, Germany **INVITED**

I will introduce the method fs-time resolved pump-probe spectroscopic ellipsometry (TSE), recently developed by us [1], as a mighty instrument to investigate the electronic structure and lattice properties of materials in great detail, going beyond many established experimental methods. TSE measures the transient complex dielectric function after optical excitation of charge carriers, which gives us a powerful tool to probe band structure, joint-density of states and transition matrix elements in various regions of the Brillouin zone as well as dynamic phenomena like carrier-carrier scattering, carrier-phonon scattering, excitation, and relaxation. As all this properties and effects in general also depend on the transient carrier density, analysis of TSE data provides vast knowledge about the electronic structure dynamics of materials, in particular valuable for fundamental theory approaches.

After excitation with an intense pump-laser, electrons and holes are created in the conduction and valence bands, respectively. These excited carriers then can scatter within the Brillion zone and interact with the lattice. This leads to dynamic carrier distribution changes in energy and momentum within time scales of fs up to ns or longer. The ellipsometry probe pulse then feels the actual energetic charge carrier distribution at a given delay time step, as expressed in changes of the dielectric function due to Pauli blocking or enabling of new transitions, energy shifts, as well as Drude response induced by these excess carriers in the respective band states. When modelling the experimentally found transient dielectric function with appropriate line shape model functions under mutual comparison with theoretically obtained data for the band structure and joint density of states, we can identify the positions of the charge carriers within the band structure in time, energy, and momentum.

Modelling TSE data is a very complex task: The spatial distribution of the excited carriers must be considered in transfer-matrix analysis, many time-delay steps have to be analysed simultaneously in model function approximation to identify positive and negative contributions as well as to obtain physically meaningful time-evolution of the parameters, and many more challenges. To circumvent the problems, we apply machine-learning based algorithm to find the best modelling of the data.

In my presentation I will introduce technical details of the method TSE, discuss modelling strategies, and give examples of processes observed in various material systems.

[1] S. Richter, M. Rebarz, O. Herrfurth, S. Espinoza, R. Schmidt-Grund, and J. Andreasson, Rev. Sci. Instrum. 92, 033104 (2021)

8:40am **EL+AS+EM-TuM-3 Evolution of Anisotropy and Order of Band-to-Band Transitions, Excitons, Phonons, Static and High Frequency Dielectric Constants Including Strain Dependencies in Alpha and Beta Phase ($Al_xGa_{1-x})_2O_3$**, ***Megan Stokey,*** *R. Korlacki, M. Hilfiker, T. Gramer, J. Knudtson,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight,* Linkoping University, Sweden*; A. Mock,* Weber State University*; A. Mauze, Y. Zhang, J. Speck,* University of California Santa Barbara*; R. Jinno, Y. Cho, H. Xing, D. Jena,* Cornell University*; E. Ahmadi,* University of Michigan*; V. Darakchieva,* Lund University, Sweden*; M. Schubert,* University of Nebraska-Lincoln

The rhombohedral alpha and monoclinic beta phases of gallium oxide both make promising candidates for ultra-wide bandgap semiconductor technology. Of particular interest are alloyed films and the evolution of anisotropic optical properties with respect to both alloy composition and strain induced effects. Here, we study alpha and beta phase $(Al_xGa_{1-x})_2O_3$ via a combined density functional theory and generalized spectroscopic ellipsometry approach across a range of alloying. Infrared-active phonon properties, static dielectric constants and midband gap indices of refraction are quantified.[1,2,3] Strain and alloying effects are shown and compared to previous theoretical works.[4] Bandgaps, excitons, and high-frequency dielectric constants are also investigated in the visible to vacuum-ultra-violet (VUV) spectral range.[5,6,7,8] We identify a switch in band order where the lowest band-to-band transition occurs with polarization along the ordinary plane in α-Ga--$_2$O-$_3$ whereas for α-Al-$_2$O$_3$ the lowest transition occurs with polarization in the extraordinary direction. With this, we present the most comprehensive picture of optical properties' evolution along composition and strain currently available.

[1] M. Stokey, R. Korlacki, *et al.,* Phys. Rev. Materials 6, 014601 (2022)

[2] M. Stokey, T. Gramer, *et al.,* Appl. Phys. Lett. 120, 112202 (2022)

[3] M. Stokey, R. Korlacki, *et al.*, "The influence of strain and composition on the infrared active phonons in epitaxial β-(AlxGa1-x)2O3 deposited onto (010) β-Ga2O3", *In Preparation*

[4] R. Korlacki, M. Stokey, A. Mock, *et al*., Rev. B 102, 180101(R) (2020)

[5] M. Hilfiker, R. Korlacki, *et al.,* Appl. Phys. Lett. 118, 062103 (2021)

[6]M. Hilfiker, R. Korlacki, *et al.,* Appl. Phys. Lett. XX, XX (2022)

[7] M. Hilfiker, U. Kilic, M. Stokey, *et al.,* Appl. Phys. Lett. 119, 092103 (2021)

[8] M. Hilfiker, U. Kilic, *et al.,* Phys. Lett. 114, 231901 (2019)

9:00am **EL+AS+EM-TuM-4 Engineering the Bi-Signate Broadband Enhanced Chirality Revealed by All Dielectric *Nanoboomerang* Structure**, ***Ufuk Kilic,*** *M. Hilfiker, A. Ruder, S. Wimer, S. G. Kilic, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

Chirality phenomenon has recently aroused remarkable interest because of its promising potential applications in optics, catalysis and sensing. However, the large-scale mismatch between the wavelength of incident circular polarized (chiral) light and the size of natural chiral crystals (such as quartz or benzyl) or small size of chiral molecules (such as DNA or proteins) led the chiral light-matter interactions to be extremely weak in nature and cannot be made tunable [1]. The recent studies showed that one can obtain strong and tunable chiral response using subwavelength scale structures so-called metamaterials. As a promising large-scale area, bottom-up 3D nanomorphology fabrication method with precise sample stage manipulation ability, the glancing angle deposition (GLAD), is envisioned as a promising route to the experimental realization of strong and tunable chiroptical responses [1].

Here, we propose a simplistic chiral-nano-platform: all-dielectric spatially coherent, superlattice type, distorted L-shape metamaterials so-called chiral *nanoboomerangs* which were fabricated using custom-built, ultra-high-vacuum electron beam evaporated GLAD instrument. The structure consists of two achiral silicon nano-columnar segments, but the sample stage is rotated prior to the fabrication of second segment. Using a Mueller matrix spectroscopic ellipsometry based chiroptical characterization method, we found that our proposed large-scale nanophotonic metamaterial platform exhibits extremely broadband, large, tunable, and bi-signate chiroptical response within the near infrared to vacuum ultraviolet spectral range. We believe that this new material platform is a strong candidate for a myriad of next generation photonic integrated technological applications including but not limited to chiral sensors, drug-delivery systems, and chiral-topological insulators.

*Reference:*

1. Kilic, U. *et al.*, Advanced Functional Materials, 31(20), 2010329, (2021).

9:20am **EL+AS+EM-TuM-5 Structural Properties and Optical Constants of $CaF_2$ at 300 K from 0.03 to 6.5 eV**, ***Jaden R. Love,*** *N. Samarasingha, C. Armenta, S. Zollner,* New Mexico State University*; H. Kim,* National Institute of Aerospace (NIA)

In this undergraduate student presentation, we describe the structural and optical properties of calcium fluoride ($CaF_2$) an insulator with an ultrawide band gap of 12 eV and a large exciton binding energy of 1 eV. $CaF_2$ has a wide range of transparency from 125 meV in the infrared to 10 eV in the ultraviolet making it an ideal substrate for optical devices. Such optical devices include actively tunable transmission filters utilizing certain phase change memory materials (PCM's) which can be used for higher resolution imaging on satellites. Most studies of the optical constants of $CaF_2$ were performed in the 1960's and are discussed in [1]. Revisiting these optical constants using modern ellipsometry equipment and specimens from different manufacturers with (100) and (111) orientation seems timely. $CaF_2$ crystallizes in the fluorite structure with space group Fm-3m and has a lattice constant of 5.4626 Å. The $Ca^{2+}$ atoms are located in the Wyckoff (4a) position at the origin. The $F^-$ atoms are at the (8c) positions (¼,¼,¼) and (¼,¼,3/4). There is a three-fold degenerate Raman-active $T_{2g}$ mode and a three-fold degenerate infrared active $T_{2u}$ mode, which splits into a transverse optical (TO) doublet and a longitudinal optical (LO) singlet. The

$T_{2u}$ mode can be observed with Fourier-transform infrared ellipsometry and described with a Lorentzian. The TO and LO energies are 261 and 477 $cm^{1-}$, respectively, with an amplitude A=4.1, a broadening of 4 $cm^{1-}$, and a high-frequency dielectric constant of 1.98[1]. A dip in the reststrahlen band is due to two-phonon absorption described with an anharmonically broadened Lorentzian. In the visible and near ultraviolet approaching 6.5 eV, normal dispersion can be described with a pole located at 7.48 eV and a Tauc-Lorentz oscillator at 20 eV. The imaginary part of the pseudo dielectric function, $\langle\varepsilon_2\rangle$ is negative above 3 eV. This indicates a surface layer of 2 to 5 nm thickness with a larger refractive index than that of the bulk substrate. We apply the $CaF_2$ optical constants to determine the thickness of an $SiO_2$ layer on the $CaF_2$ substrate.

[1] D. F. Bezuidenhout in Handbook of Optical Constants of Solids II, edited by E. D. Palik

(Academic, San Diego, 1998).

9:40am **EL+AS+EM-TuM-6 Optical Dielectric Function of a Solution-Processable Thiazolothiazole Thin Films Determined by Spectroscopic Ellipsometry**, ***Nuren Shuchi,*** *J. Mower, V. Stinson, M. McLamb, G. Boreman, M. Walter, T. Hofmann,* University of North Carolina at Charlotte

Fluorescent molecules are ubiquitous in contemporary technologies and can be found for instance in energy-conversion devices [1], sensors [2], and are used for biological imaging techniques [3]. Recently, families of fluorescent molecules which combine multiple functionalities have gained considerable attention [4]. Significant progress has been made in the field of molecular electronics due to the advent of unique oligothiophenes [5] and thiadiazolobithienyl dyes [6]. We have synthesized solution-processable, 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole (TTz) dyes for thin film organic electronics applications. The TTz dyes were synthesized by refluxing 4-pyridinecarboxaldehyde, 4-(dibutylamino)benzaldehyde, and dithiooxamide in 40 mL of anhydrous dimethylformamide for 6 hours at 120 °C. The reaction solution was chilled overnight and crude precipitate was collected using vacuum filtration and rinsed with dimethyl sulfoxide and water. The isolated product was purified using silica gel column chromatography (Silica Flash M60) with a 1:1 hexanes/chloroform mixture. <1,0,0> Si wafers were cut to approximately 20 mm x 15 mm and sonicated in acetone, deionized water, and isopropyl alcohol for 15 minutes. The wafers were dried with compressed nitrogen gas and treated with UV / ozone for 15 minutes. The Si wafers and a 16.1 g/L 1,2-dichlorobenzene solution of the thiazolothiazole dye were heated to 55 °C in a nitrogen glove box. While in the glove box, 90 µL of the TTz solution was spin coated onto each Si wafer at 2000 RPM for 30 seconds. The wafers were heated to 110 °C for 20 minutes and stored in the glove box away from light. In this presentation, we will discuss spectroscopic ellipsometry data obtained from a 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole thin films deposited by spin coating on a silicon substrate in the spectral range from 354 nm to 1907 nm. The ellipsometric data were analyzed using a stratified layer model composed of thiazolothiazole thin film, native $SiO_2$ oxide, and Si substrate. The model dielectric function of the thiazolothiazole thin film was composed of a series of Tauc-Lorentz and Gaussian oscillators. The best-model calculated data are rendering the experimental data very well. Obtained transition energies will be reported and compared with those of related thiazolothiazole dyes. **References:** [1] J. Am. Chem. Soc. **133**, 20009 (2011). [2] Chem. Soc. Rev. **40**, 2222 (2011). [3] BMC Systems Biology **2**, 1(2008). [4] CHEM-EUR J. **19**, 2582 (2013). [5] J. Phys. Chem. Lett. **9**, 1958 (2018). [6] Sci. Rep. 6, 18870 (2016).

11:00am **EL+AS+EM-TuM-10 Bandgap Engineering of Polycrystalline Ge-doped $Sb_2Se_3$ Thin-Film: Surface and Optical Properties**, ***Sanghyun (Philip) Lee,*** University of Kentucky*; M. McInenery,* Rose-Hulman Institute of Technology

Antimony Chalcogenide, $Sb_2(S_x,Se_{1-x})_3$ is a third-generation thin-film photovoltaic device. $Sb_2(S_x,Se_{1-x})_3$ solar cells have received growing attention due to their favored properties with <9.2 % efficiency. In particular, $Sb_2(S,Se)_3$ has a high absorption coefficient at visible light (>$10^5$ $cm^{-1}$), tunable bandgap (1.0 eV – 1.7 eV), stable upon exposure to sunlight under ambient conditions.

For the optimization of bandgap of $Sb_2Se_3$ alloy films, Ge-doped $Sb_2Se_3$ thin-film for solar cells applications have been studied with various compositions and doping concentrations, showing different crystallization, surface, and optical characteristics. $Sb_2Se_3$ thin-films are crystalline as deposited and on heating with orthorhombic structures. As a few molar percent of Ge doped into $Sb_2Se_3$ (<15 %) films (GeSbSe), polycrystalline films are formed upon annealing above 200 - 250 C, demonstrating no significant dependence of lattice constant on the Ge doping level. However, most GeSbSe studies are focused on amorphous $Sb_2Se_3$ films doped with higher Ge concentration (> 15 %).

In this contribution, we have fabricated and studied the bandgap energy and surface properties of polycrystalline GeSbSe thin-films (<15 %) for the application to the photovoltaic absorber. We investigated critical optical properties of absorption coefficient and engineered optical bandgap of films grown at different temperatures. Optical responses are explored with UV-Vis spectrometer. Moreover, scanning electron microscopy and Energy-dispersive X-ray spectroscopy are used to confirm optical bandgap, surface structures, and chemical composition of GeSbSe thin-films grown by Vapor Transport Deposition at different film growth temperatures. The optimum optical characteristics of thin-film absorber materials depend on film surface microstructure, which in turn affects the overall optical behaviors of GeSbSe films.

Ge-doped $Sb_2Se_3$ thin-films (<15 %) are polycrystalline with thickness around 1 um grown at 500 C and 520 C. As the deposition temperature increases from 500 C to 520 C, uniform grains of approximately 0.9 um at 500 C become mixed grains of larger (~6 um) and smaller grains (~0.9 um), revealed by Scanning Electron Microscopy characterization. The surface morphology becomes smooth (500 C) to irregularly rougher (520 C). For the characterization of optical properties, the absorption coefficient is >$10^5$/cm near 600 nm for both films. Based on the widely used Tauc's relation, the optical bandgap of Ge-doped $Sb_2Se_3$ thin-film absorbers is extracted as 1.15 eV and 1.23 eV for samples grown at 500 C and 520 C, respectively.

11:20am **EL+AS+EM-TuM-11 Optical Properties of Orthorhombic $LiGa0_2$ from Far-Infrared to Vacuum Ultraviolet**, ***Teresa Gramer,*** *E. Williams, M. Stokey, R. Korlacki, U. Kilic, M. Hilfiker, M. Schubert,* University of Nebraska - Lincoln

Within the $Li_2O$-$Ga_2O_3$ oxide system, $LiGaO_2$ (LGO) and multiple phases of $Ga_2O_3$ (GO) are prospective ultra-wide bandgap metal oxides for electronic and optoelectronic applications [1]. While both GO and LGO have recently been identified to most likely trap holes and which makes achievement of sufficient p-type conductivity difficult [2], LGO is particularly promising as a substrate for heteroepitaxial growth of GaN due to very small lattice mismatch (<1%), and a composite LGO/β-GO substrate has also been demonstrated [3]. Here, we provide a comprehensive study of the fundamental optical and phonon mode properties of high-quality single-crystals of LGO using generalized spectroscopic ellipsometry in combination with hybrid-level density functional theory calculations that covers the optical properties in the far-infrared to vacuum ultraviolet spectral range. In the mid- to far-infrared range, we identify all 33 infrared-active pairs of transverse and longitudinal optical phonon modes. We derive the anisotropic mid-band gap indices of refraction and static dielectric constants. In the visible to vacuum ultraviolet spectral range we identify band-to-band transitions and discuss near band-gap excitonic contributions. We compare the obtained results with the previous experimental and theoretical studies. [4,5,6]

[1] A review of band structure and material properties of transparent conducting and semiconducting oxides: $Ga_2O3$ , $Al_2O3$ , $In_2O3$ , ZnO, $SnO_2$, CdO, NiO, CuO, and $Sc_2O3$ , Joseph A. Spencer, Alyssa L. Mock, Alan G. Jacobs, Mathias Schubert, Yuhao Zhang, and Marko J. Tadjer , Applied Physics Reviews 9, 011315 (2022)

[2] Self-trapped holes and polaronic acceptors in ultrawide-bandgap oxides, John L. Lyons, Journal of Applied Physics 131, 025701 (2022)

[3] Composite substrate $LiGaO_2$ (0 0 1) β-$Ga_2O3$ (1 0 0) fabricated by vapor transport equilibration, Zhang, Jungang & Xia, Changtai & Li, Shuzhi & Xu, Xiaodong & Wu, Feng & Pei, Guangqing & Xu, Jun & Zhou, Shengming & Deng, Qun & Xu, Wusheng & Shi, Hongsheng. Mater. Lett. 60. 3073-3075. (2006)

[4] Optical properties of lithium gallium oxide, S. Tumenas, P. Mackonis, R. Nedzinskas, L. Trinkler, B. Berzina, V. Korsaks, L. Changc, M.M.C. Chou , Applied Surface Science, Volume 421, Part B. (2017)

[5] Quasiparticle self-consistent GW band structures and high-pressure phase transitions of $LiGaO_2$ and $NaGaO_2$, Santosh Kumar Radha, Amol Ratnaparkhe, and Walter R. L. Lambrecht, Physical Review B 103, 045201 (2021)

[6] Piezoelectric, Elastic and Dielectric Properties of $LiGaO_2$, Satoshi Nanamatsu et al, Jpn. J. Appl. Phys. 11 816 (1972)

11:40am **EL+AS+EM-TuM-12 Optical and X-ray Characterization of Ge-Sn Alloys on GaAs**, ***Haley Woolf**, C. Emminger, C. Armenta,* New Mexico State University*; M. Kim,* QuantTera*; S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe the optical and x-ray characterization of a thick $Ge_{1-y}Sn_y$ alloy grown on GaAs by chemical vapor deposition. From (224) x-ray reciprocal space maps we find that the alloy layer is grown pseudomorphically on the GaAs substrate. Therefore, we can use (004) rocking curves and reciprocal space maps to determine the alloy composition based on Vegard's Law. We find y=0.012.

For ellipsometry measurements, we first cleaned the surface ultrasonically with water and isopropanol to remove adsorbed organic overlayers and a portion of the native oxide. The remaining native oxide was found to be 2.6 nm thick. We then acquired the ellipsometric angles ψ and Δ from 0.5 to 6.5 eV photon energy and 60 to 75° incidence angle using a vertical variable angle of incidence ellipsometer (VASE) equipped with a computer-controlled Berek wave plate compensator. Due to the low tin content, these ellipsometric angles and the resulting pseudo-dielectric function could be described very well using a four-layer model, consisting of a GaAs substrate, a pure Ge layer, $GeO_2$ oxide, and air as the ambient. This results in an epilayer thickness of 1600 nm.

After fixing the thickness, we also obtained the dielectric function ε of the epitaxial $Ge_{1-y}Sn_y$ layer from a point-by-point fit. This is very similar to that of bulk Ge. The second derivative $d^2\varepsilon/dE^2$ was fitted with analytical line shapes to determine the critical point parameters of the alloy (amplitude, energy, broadening, and phase angle). The energy was compared with predictions from continuum elasticity theory based on established deformation potentials for Ge.

12:00pm **EL+AS+EM-TuM-13 Zinc Gallate ($ZnGa_2O_4$) Epitaxial Thin Films: Determination of Optical Properties and Bandgap Estimation Using Spectroscopic Ellipsometry**, *S. Bairagi, J. Chang, C. Hsiao, R. Magnusson, J. Birch,* Linköping University, Sweden*; **Jinn P Chu**,* National Taiwan University of Science and Technology, Taiwan*; F. Tarntair,* National Yang Ming Chiao Tung University, Taiwan*; R. Horng,* National Yang Ming Chiao Tung University, Taiwan*; K. Järrendahl,* Linköping University, Sweden

Very high quality Zinc gallate (ZGO) epitaxial thin films were grown on c-plane sapphire substrates by Metal-Organic Chemical Vapor Deposition and investigated using Spectroscopic Ellipsometry (SE). Two or more samples were grown with identical growth conditions but different growth times to obtain samples with similar crystallographic and optical properties but different thicknesses. Their thickness, roughness and optical properties were then determined using a Multiple Sample Analysis (MSA) based approach in tandem by the regression analysis of the optical model and measured data for all samples. Another set of ZGO samples were grown for the same growth time but etched using ion-bombardment for different time durations to achieve different thicknesses. These samples were also analyzed by SE using MSA and it was observed that etching times of 1 – 4 minutes had no discernible impact on the material's optical properties. It was also observed that both sets of samples exhibited identical optical properties and thus could be described using the same optical model, thereby showcasing the robustness of the MSA model. Line shape analysis of resulting absorption coefficient dispersion revealed that ZGO exhibited both direct and indirect interband transitions. A modified Cody formalism was employed to determine their optical bandgaps, resulting in a direct bandgap of 5.07 ± 0.015 eV and indirect bandgap of 4.72 ± 0.015 eV. These values were compared to values obtained using other popular bandgap extrapolation procedures to find which technique resulted in the most linear line shape. In a subsequent study, the first set of samples was annealed to different temperatures and their optical properties were analyzed using SE. It was observed that the onset of absorption and hence the optical bandgap blue-shifted to higher photon energies as the annealing temperature was increased from 800° C to 1100° C. This was a consequence of inter-diffusion between the ZGO thin film and sapphire substrate, resulting in the formation of an epitaxial β-(Al, Ga)O intermediate layer between the two, and modification of ZGO to Zn(Al, Ga)O due to diffusion of Al. Post analysis it was observed that the formation of β-(Al, Ga)O intermediate layer began already at 800° C and led to an increase in the overall film thickness with increasing annealing temperatures. The direct and indirect optical bandgaps for the Zn(Al, Ga)O thin film were determined to be 5.10, 5.19, 5.73 eV and 4.80, 4.87, 5.45 eV for 800, 950 and 1100° C, respectively and the increase is attributed to the diffusion of Al from the sapphire substrate.

# Author Index

## Bold page numbers indicate presenter