Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EL+MS+SS-MoA

Advancing Metrology and Characterization to Enable Atomic Scale Processing

Moderators: Steven M. George, University of Colorado at Boulder, **Rudy Wojteki**, IBM Almaden Research Center

1:40pm **AP+AS+EL+MS+SS-MoA-1 Nanoscale Chemical Analysis and Mapping of Atomic and Molecular Scale Processes via Infrared Photo-Induced Force Microscopy*, Sung Park,*** Molecular Vista **INVITED**

As semiconductor device feature sizes move beyond the sub-7 nm technology node, atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) are being adopted to gain control over key processing parameters.These techniques are commonly combined with thin polymer barrier layers such as self-assembled monolayers (SAM) that are selectively located to achieve area selective deposition or etching. In protein and DNA chips, monolayers of specific molecules are engineered and patterned to guide the target molecules to specific locations.Common to these devices and processes are the atomic scale thicknesses, nanoscale lateral dimensions, and the combination of multiple materials consisting of organic and inorganic compounds, metals, and 1D/2D materials which demand new metrology and characterization techniques to assess and monitor these advanced processing techniques.Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) to achieve nanoscale chemical analysis via localized IR absorption spectrum and mapping of heterogeneous materials on the surface of a sample (with sub-5 nm spatial resolution).The spectroscopic capability is useful for ascertaining the presence and quality of the molecular species. The mapping capability is useful for investigating surface functionalization and chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, sequential infiltration synthesis, and a variety of area-selective deposition techniques. PiFM applications on various atomic and molecular scale processes will be presented.

[1] D. Nowak et al., Sci. Adv. 2, e150157 (2016).

2:20pm **AP+AS+EL+MS+SS-MoA-3 Area-Selective Deposition/Patterning of Boron Carbide Layers: Etch Studies*, Raja Sekhar Bale,*** *R. Thapa, A. Caruso,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation*; M. Paquette,* University of Missouri-Kansas City

The semiconductor industry is pushing the boundaries of device scaling by way of novel processing methods and increasingly complex patterning schemes. This requires a variety of functional and patterning-assist materials as well as advanced deposition techniques. For years, silicon-based materials have been used to meet these needs; however, these alone cannot fulfill the range of material requirements moving forward. Boron carbide has shown promise due to its compelling dielectric, thermal, mechanical, chemical, and etch properties. Toward applying this material to next-generation integration schemes, we have been exploring the potential of going beyond traditional growth processes (e.g., plasma-enhanced chemical vapor deposition) and investigating innovative area-selective atomic layer deposition (AS-ALD) strategies. Herein we explore schemes for the selective dielectric on metal/dielectric deposition of boron carbide using monolayer and layer-by-layer methods. In particular, we focus on etch studies (wet and dry) toward understanding the stability and removal of these layers. X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques are employed for the characterization and imaging of the resulting surfaces.

2:40pm **AP+AS+EL+MS+SS-MoA-4 Smoothing of Surfaces by Atomic Layer Deposition and Etching***, S. Gerritsen, N. Chittock, V. Vandalon, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; E. Kessels,* ***Adrie Mackus,*** Eindhoven University of Technology, The Netherlands

With critical dimensions scaled down to the nanoscale in current electronics, surface and interface roughness increasingly limit device performance. In this work, we use simulations and experiments to explore whether atomic layer deposition (ALD), atomic layer etching (ALE) and combinations of these techniques can be used to smoothen surfaces, while processing materials with excellent uniformity and atomic scale control. The smoothing is experimentally demonstrated by atomic force microscopy and transmission electron microscopy analysis.

Many previous studies have shown that ALD and ALE can smoothen surfaces,[1,2] but the extent of smoothing has not been systematically characterized and the mechanisms of smoothing are only partly understood. In our studies, finite difference simulations were performed that describe ALD/ALE as a uniform front from which the deposition/etching propagates isotropically at every point. Al_2O_3 ALD experiments using TMA and O_2 plasma validated this uniform front propagation model. A smoothing rate of $5.5\cdot10^{-3}$ nm RMS roughness reduction per nm of deposition was determined, revealing that significant smoothing by ALD requires relatively thick films (e.g. > 20 nm).

Al_2O_3 ALE from TMA and SF_6 plasma[3] resulted in a larger roughness reduction of $9.8\cdot10^{-3}$ nm/nm, which is explained by considering that the fluorination of the surface depends on the local curvature, such that peaks are smoothed more than valleys. In other words, for ALE two mechanisms contribute to the smoothing, i.e. uniform front propagation and curvature-dependent fluorination. In order to benefit from the enhanced smoothing by ALE, especially combinations of ALD and ALE in supercycle recipes can be very effective in smoothing surfaces, as will be highlighted in the contribution.

(1)Elam *et al.*, *Thin Solid Films***414**, 43 (2002)

(2)Zywotko *et al.*, *J. Vac. Sci. Technol. A* **36**, 061508 (2008)

(3)Chittock *et al.*, *Appl. Phys. Lett.* **117**, 162107 (2020)

3:00pm **AP+AS+EL+MS+SS-MoA-5 Thermal Atomic Layer Etching of Amorphous Aluminum Nitride Using Sf_6 Plasma and $Al(Ch_3)_3$*, Haozhe Wang,*** *A. Houssain, D. Catherall, A. Minnich,* California Institute of Technology

We report the thermal atomic layer etching (ALE) of amorphous aluminum nitride using sequential exposures of low-power SF_6 plasma and trimethylaluminum ($Al(CH_3)_3$, TMA). ALE was observed at temperatures greater than 200 °C, with etch rates varying with temperature from 0.1 Å/cycle at 200 °C to 1.9 Å/cycle at 300 °C, as measured using ex-situ ellipsometry. The self-limiting nature of the reactions was established by verifying that no etching occurred with only SF_6 or TMA. The etched surface was characterized using atomic force microscopy and x-ray photoemission spectroscopy. After 50 cycles of ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a~35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and semiconductor devices.

3:20pm **AP+AS+EL+MS+SS-MoA-6 Thermal Atomic Layer Etching using MoF6-H2O precursors*, Anil Mane,*** *J. Elam,* Argonne National Laboratory, USA

Well controlled atomic layer etching (ALE) processing is needed for the creation of next generation complex 3D devices. A simple semiconductor processing compatible thermal ALE method is preferred for the process integration point of view. Recently we have developed the MoF6-H2O precursors based etching methods for the etching of atomic layer deposited (ALD) TiO2, Ta2O5 and MoS2 in a precise controlled manner. The etch rate and etch behavior of these materials mainly controlled by processing temperature (100-325ºC) and precursors dose times. The MoF6-H2O etching process of these ALD grown TiO2, Ta2O5 and MoS2 was studied by in-situ methods such as infrared spectroscopy (FTIR), quartz crystal microbalance (QCM), and spectroscopic ellipsometry (SE). Additionally, at present we have also developed novel in-situ calorimetry method to measure chemical reaction heat in ALE precursor's reaction. Here some of latest results on this in-situ ALE-calorimetry method will also be presented.

4:00pm **AP+AS+EL+MS+SS-MoA-8 The Thinner, the Better - Characterization of Ultra-Thin Films by Low Energy Ion Scattering (Leis)*, Thomas Grehl,*** IONTOF GmbH, Germany **INVITED**

Current and future thin film processes require quantitative characterization from the early phases of film growth to complex film stacks with a total thickness of only a few nm. While many surface analytical techniques are challenged by this requirement, Low Energy Ion Scattering (LEIS) analysis is ideally suited for ultra-thin film and sub-monolayer characterization. The key property is its single atomic layer information depth.

By scattering noble gas ions from the surface of the sample, LEIS determines the elemental composition of the surface of the outermost atomic layer. Nucleation processes and layer closure are investigated, but also diffusion from the bulk towards the surface can be studied with in-situ sample heating and continuous monitoring of the surface composition.

In addition to the surface composition, also the distribution of elements over the first few nm of the sample is contained in the spectra. The so-called "in-depth information" is acquired in a virtually non-destructive way, avoiding sputtering and therefore the long measurement times and artefacts associated with it. For sufficiently thin films, the depth resolution is only a few Å. This allows to study the development of the film thickness while also monitoring film closure to determine the growth mode.

In some cases, low energy noble gas sputtering is applied to extend the depth range beyond a few nm or to handle complex materials where "in-depth" and surface information cannot be deconvoluted.

In this contribution, we will highlight a number of examples from quite different materials and film systems. These will be used to illustrate how LEIS is applied in practical way. We will show how LEIS contributes unique information for modern ultra-thin film characterization.

4:40pm **AP+AS+EL+MS+SS-MoA-10 Intrinsic Area Selective Atomic Layer Deposition of MoS_2 Thin Films***, J. Soares, **Wesley Jen**, S. Hues,* Boise State University*; J. Wensel,* Micron Technology Inc*; E. Graugnard,* Boise State University

As the critical dimensions in today's semiconductor devices continues to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS_2) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS_2 on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS_2 films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of S = 0.94 after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS_2 ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS_2 modes and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) elemental mapping, which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

5:00pm **AP+AS+EL+MS+SS-MoA-11 In Situ Measurements of Surface and Film Stress during Atomic Layer Deposition of Al_2O_3 and AlF_3 using Wafer Curvature Techniques***, **Ryan B. Vanfleet**, E. Sorinto, A. Cavanagh, V. Bright, S. George,* University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The in situ measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress then decreases with increasing deposition temperature. These in situ temperature-dependent Al_2O_3 ALD film stresses are in good agreement with ex situ film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These in situ measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional in situ measurements have explored the surface and film stresses during AlF_3 ALD using TMA and HF as the reactants. AlF_3 ALD showed similar surface stress behavior to Al_2O_3 ALD. The TMA exposure again results in a compressive stress attributed to repulsion between surface methyl groups. The HF exposure then removes the methyl groups and releases the compressive stress. At AlF_3 ALD temperatures between 150-200°C, the compressive surface stress resulting from the TMA exposures is ~0.45 N/m. In marked contrast to Al_2O_3 ALD, AlF_3 ALD displayed no film stress during film growth. This lack of film stress in AlF_3 ALD films may be related to the nature of the AlF_3 ALD film as a molecular solid.

[1]O.M.E. Ylivaara et al., *Thin Solids Films* **552**, 124 (2014)

Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA

Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES***, **David Cant**,* National Physical Laboratory, UK **INVITED**

'Soft' x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from 'soft' XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of 'soft' XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a 'universal' calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES***, **Thierry Conard**, A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as TiN/HfO_2/SiO_2/Si as well as more complex stacks such as TaN/TiAl/TiN/HfO_2/SiO_2/Si or W/TiN/HfO_2/SiO_2/Si. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

References

[1]https://www.ulvac-phi.com/en/products/xps/quantes/

[2]https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument

[3]https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab

2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability***, P. Dietrich, **Andreas Thissen**,* SPECS Surface Nano Analysis GmbH, Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable***, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*; **Christopher Moffitt**,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the “tool”. In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable – delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***, **Alberto Herrera-Gomez**, D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

[1] D. Cabrera-German, G.-B. Dulce-Maria, M. Mayorga-Garay, O. Cortazar-Martinez, J.-A. Torres-Ochoa, A. Carmona-Carmona, A. Herrera-Gomez, Peak and background parameters of the 2p core level of the pure first row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[2] D.-M. Guzman-Bucio, A. Carmona-Carmona, M.A. Gonzalez-Reyna, A. Herrera-Gomez, Peak and background parameters of the 3d core level of the pure second row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[3] A. Herrera-Gomez, D. Cabrera-German, A.D.A.D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, L. Gomez-Muñoz, L.G.M. Herrera-Gomez, Alberto., Dagoberto Cabrera-German., Anthony D. Dutoi., Milton Vazquez Lepe., Servando Aguirre-Tostado., Piero Pianetta., Dennis Nordlund., Orlando Cortazar-Martinez., Alejandro Torres-Ochoa., Oscar Ceballos-Sanchez., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. https://doi.org/10.1002/sia.6364.

[4] J.E. Castle, a. M. Salvi, Interpretation of the Shirley background in x-ray photoelectron spectroscopy analysis, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 19 (2001) 1170. https://doi.org/10.1116/1.1378074.

4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***, **Lev Gelb**, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide “fractional composition vs ion dose” profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm. The only required inputs to the calculation are the “fractional composition” profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***, **David Morgan,*** Cardiff University, UK

As XPS systems become ever more user-friendly, with “load-point-click-report” type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

[1] L. Edwards, P. Mack and D. J. Morgan, “Recent advances in dual mode charge compensation for XPS analysis”. Surface and Interface Analysis, 51 (2019) 925-933
[2] R. McLaren, G. Owen and D. J. Morgan, “Analysis Induced Reduction of a Polyelectrolyte”, Results in Surfaces and Interfaces, (2021) 100032
[3] G. Beamson and D. Briggs, “High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database,” Wiley, Chichester, 1992.

4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed,*** National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene’s inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 “Surface Chemical Analysis”.

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

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, $<\varepsilon_2>$ 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$_2$Se$_3$ 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$_2$Se$_3$ alloy films, Ge-doped Sb$_2$Se$_3$ thin-film for solar cells applications have been studied with various compositions and doping concentrations, showing different crystallization, surface, and optical characteristics. Sb$_2$Se$_3$ thin-films are crystalline as deposited and on heating with orthorhombic structures. As a few molar percent of Ge doped into Sb$_2$Se$_3$ (<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$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$O-Ga$_2$O$_3$ oxide system, LiGaO$_2$ (LGO) and multiple phases of Ga$_2$O$_3$ (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$_2$O3 , Al$_2$O3 , In$_2$O3 , ZnO, SnO$_2$, CdO, NiO, CuO, and Sc$_2$O3 , 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$_2$O3 (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.

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL1+AS+EM-TuA

Emerging Technological Advances and Breakthroughs of Spectroscopic Ellipsometry

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

2:20pm **EL1+AS+EM-TuA-1 Terahertz to Vacuum Ultraviolet Ellipsometry Characterization of Spin, Lattice, Strain, Free Charge Carrier, Dielectric Constants, Exciton and Band-to-Band Transition Properties in Ultrawideband Gap Alpha and Beta Aluminum Gallium Oxide Semiconductor Alloys***, **Mathias Schubert**, R. Korlacki, M. Stokey,* University of Nebraska-Lincoln*; A. Mock,* Weber State University*; M. Hilfiker,* University of Nebraska-Lincoln*; J. Knudtson,* University of Nebraska-Lincoln, USA*; U. Kilic,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight, P. Kuehne,* Linkoping University, Sweden*; V. Darakchieva,* Lund University, Sweden **INVITED**

Two phases of ultrawideband gap semiconductor gallium oxide emerge in composition with aluminum, the rhombohedral alpha and monoclinic beta phase of AlGaO. Progress in epitaxial deposition provides quality materials investigated currently with large efforts. Both phases permit access to ultrawideband gap properties reaching approximately 9 eV with sapphire. We employ a wide range of ellipsometry techniques covering 100 GHz to approximately 9.5 eV, including magnetic fields and density functional theory calculations. We provide an overview of current knowledge of properties for both compounds, discussing strain-stress relationships, evolution of phonon mode and band to band transition behaviors, dielectric constants, indices of refraction, anisotropy, and free charge carrier and defect properties [1-8]. We report on a new hyperbolic shear polariton formation in monoclinic Ga2O3 [9]. We also report on initial results of our newly developed instrumental approach for defect characterization in quantum materials, THz electron paramagnetic resonance ellipsometry for ultrahigh field and high resolution frequency spin detection and analysis in epitaxial semiconductor layer systems [10]. [1] M. Stokey et al., Phys. Rev. Materials 6, 014601 (2022). [2] M. Hilfiker et al., Appl. Phys. Lett. 118, 062103 (2021). [3] M. Hilfiker, U. Kilic, M. Stokey, R. Jinno, Y. Cho, H. Grace Xing, D. Jena, R. Korlacki, and M. Schubert, Appl. Phys. Lett. 119, 092103 (2021). [4] R. Korlacki, M. Stokey, A. Mock, S. Knight, A. Papamichail, V. Darakchieva, and M. Schubert, Phys. Rev. B 102, 180101(R) (2020). [5] P. Gopalan, S. Knight, A. Chanana, M. Stokey, P. Ranga, M. Scarpulla, S. Krishnamoorthy, V. Darakchieva, Z. Galazka, K. Irmscher, A. Fiedler, S. Blair, M. Schubert, and B. S. Rodriguez, Appl. Phys. Lett. 117, 252103 (2020). [6] M. Hilfiker, U. Kilic, A. Mock, V. Darakchieva, S. Knight, R. Korlacki, A. Mauze, Y. Zhang, J. Speck, and M. Schubert, Appl. Phys. Lett. 114, 231901 (2019). [7] J. A. Spencer, A. L. Mock, A. G. Jacobs, M. Schubert, Y. Zhang, and M. J. Tadjer, Appl. Phys. Rev. 9, 011315 (2022). [8] R. Korlacki, J. Knudtson, M. Stokey, M. J. Hilfiker, V. Darakchieva, and M. Schubert, Appl. Phys. Lett. 120, 042103 (2022). [9] N. Passler, X. Ni, G. Hu, J. R. Matson, M. Wolf, M. Schubert, A. Alù, J. D. Caldwell, T. G. Folland, and A. Paarmann, Nature 602, 595 (2022). [10] M. Schubert, S. Knight, S. Richter, P. Kuehne, V. Stanishev, A. Ruder, M. Stokey, R. Korlacki, K. Irmscher, P. Neugebauer, and V. Darakchieva, Appl. Phys. Lett. 120, 102101 (2022).

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL2+EM-TuA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

4:20pm **EL2+EM-TuA-7 A Study of Wire Grid Polarizers with Mueller Matrix Ellipsometry***, T. Gholian Avval, M. Linford,* Brigham Young University*; N. Keller, **G. Andrew Antonelli**,* Onto Innovation, Inc.

Wire grid polarizers are essential optical components used in a wide variety of optical systems, from AR/VR to medical imaging to optical measuring systems. Physical properties of the polarizer, such as groove height and width all impact the polarizer's efficiency. Here we show how a wire grid polarizer can be characterized non-destructively in the fabrication process with Mueller Matrix ellipsometry and RCWA-based analysis. Using this methodology, physical properties like grating profile, height, pitch, material thicknesses and even grating tilt can be measured non-destructively and inline to provide process control.

4:40pm **EL2+EM-TuA-8 Temperature Dependence of the Direct Band Gap of InSb from 80 to 700 K***, **Melissa Rivero Arias**, N. S. Samarasingha, C. Emminger, S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe measurements of the dielectric function of bulk InSb near the direct band gap using Fourier-transform infrared (FTIR) spectroscopic ellipsometry from 80 to 800 K in an ultra-high vacuum (UHV) cryostat with diamond windows. Indium antimonide (InSb) is the zinc blende compound semiconductor with the smallest direct band gap (ε_0= 0.18 eV at room temperature) due to its heavy elements and the large resulting spin-orbit splitting and Darwin shifts. It also has a low melting point of 800 K. Previously, the bandgap of InSb has mostly been measured optically up to room temperature and estimated from Hall effect measurements of the effective mass up to 470 K. Ellipsometry measurements of the direct gap of InSb have been described at 300 K. Calculations indicate that InSb should undergo a topological phase transition from semiconductor to semi-metal (and topological insulator) at 600 K. It is interesting to see in the data if this transition occurs below the melting point of InSb.

5:00pm **EL2+EM-TuA-9 Coherent Acoustic Phonon Oscillations in Ge Using Pump-Pulse Time-Resolved Spectroscopic Ellipsometry***, **Carlos Armenta**,* New Mexico State University*; M. Zahradnik,* ELI Beamlines, Czechia*; C. Emminger,* Humboldt University Berlin, Germany*; S. Espinoza, M. Rebarz, J. Andreasson,* ELI Beamlines, Czechia*; S. Zollner,* New Mexico State University

Photoexcitation of bulk materials can create hot charge carriers that relax by transferring energy to the lattice, hence exciting phonons in the process. By photoexciting the material through femtosecond laser pulses, coherent acoustic phonon (CAP) oscillations at picosecond time scales are generated via this method. These CAP oscillations are related to an increase in charge carrier density, as well as strain triggered by the laser pulse, however details of this relationship are scarce in the literature. CAP oscillations affect the pseudo-dielectric function (DF) of the material, which makes time-resolved spectroscopic ellipsometry ideal to understand the processes in hand.

The present work aims to describe the relationship between CAP oscillations and charge carrier density, as well as surface orientation dependence via femtosecond pump-probe ellipsometry of Ge. Photoexcitation is induced by 800 nm laser pump pulses at different intensities, generating a strain pulse that travels normal to the surface within the ~200 nm penetration depth in the semiconductor. Measurements in Ge at (100), (110), and (111) orientations and charge carrier concentrations ranging from $\sim 7.5\times10^{20}$ cm^{-3} to $\sim 3.5\times10^{21}$ cm^{-3} were performed. The behavior of these oscillations is characterized by analyzing the changes in the pseudo-DF of Ge as a function of the delay time between the pump and probe pulse. Analyzing the E1 and E1+Δ1 critical points (CP) and the variation of their parameters (energy, broadening, amplitude, and phase) with delay time, the behavior of phonon oscillations can be studied.

In order to determine these parameters, second derivatives of the pseudo-DF were calculated using a linear filter technique based on extended Gauss (EG) functions. The periods of these oscillations are deduced by tracking the energy of these CPs as a function of time

5:20pm **EL2+EM-TuA-10 Time-Resolved Spectroscopic Ellipsometry Helped by Imaging Spectroscopic Ellipsometry***, **Shirly Espinoza**,* ELI Beamlines, Czechia

Thanks to femtosecond pulsed lasers, at ELI Beamlines in the Czech Republic, we developed a time-resolved femtosecond ellipsometry technique, where a pump beam from any wavelength between 200 nm and 2000 nm excites a material; and a second pulse, the probe beam, with a continuous spectrum from 350 nm to 750 nm measures the dielectric function of that material. The pump and the probe beam can be separated in time from femtoseconds to nanoseconds generating a time-scan of the relaxation processes that happens in the material when it returns to its original unexcited state.

This time-resolved pump-probe ellipsometry technique is available to the scientific community through a yearly call for user proposals. We then get the opportunity to measure different type of materials from thin films to crystals of semiconductors and metals including 2D materials and organic samples deposited on metal layers. By imaging ellipsometry, the sample inhomogeneity, roughness and optical properties prior and after the pump-probe measurement are diagnosed. A discussion about newly imaging-analyzed samples that were and will be study by pump-probe ellipsometry will be presented.

Spectroscopic Ellipsometry Focus Topic

Room Ballroom A - Session EL-TuP

Spectroscopic Ellipsometry Poster Session

EL-TuP-2 Unraveling the Ultra-Violet Active Chiroptical Response by ZrO_2 Helical Nanostructures, ***Ufuk Kilic***, *M. Hilfiker, S. Wimer, S. G. Kilic, C. Argyropoulos, E. Schubert, M. Schubert,* University of Nebraska-Lincoln

Chirality, the handedness of a material, which cannot be made superimposable on its mirror image by using simple symmetry operations (ie. translation or rotation). This symmetry breaking phenomenon has recently gained unprecedented attention due to its pivotal roles in the sub-fields of physics, chemistry, biology, and pharmacy [1]. Briefly, chiral-materials have the differential absorption properties of two possible spin states of photons: left- and right-circularly polarized light. However, the chirality of molecules found in nature is very weak and almost impossible to spectrally tailor their response. Moreover, the absorption bands of optically active chiral molecules typically appear in the deep ultraviolet part of the spectrum [2]. Using metamaterial platforms to sense these chiral molecules is challenging because majority of them are designed to operate in the infrared to visible spectral range [1,3,4]. The use of ultra-wide band gap metal oxides in the fabrication of nanostructures has been seldom discussed in the literature and investigations on their chiral properties remained almost untouched [4].

Our theoretical studies showed that one can get deep-ultra violet strong chirality response from ZrO_2 helical nanostructure design. Hence, using a recently emerging bottom-up, wafer-scale, 3D nano-morphology fabrication technique so-called glancing angle deposition, we successfully fabricated helical nano-structures from ZrO_2 ultra-wide band gap metal-oxide. By using the Mueller matrix generalized spectroscopic ellipsometry technique, the experimental chiroptical characterization was performed and verified the theoretically predicted existence of UV-active chiroptical response from the proposed ZrO_2 nanohelical metamaterial platform.

We envision that such nanostructure design with large chirality signals in the UV range of wavelengths, where the electronic transitions for biomolecules often occur can open a new avenue for their potential use in the next generation chiral sensor, bio-imaging, polarization bio-encryption or chiral-photonics device applications.

References:

[1] Hentschel, Mario, et al. *Science advances* 3.5 (2017): e1602735.

[2] Meierhenrich, Uwe J., et al. , *Angewandte Chemie International Edition* 49.42 (2010): 7799-7802.

[3] Kilic, Ufuk, et al., *Advanced Functional Materials* 31.20 (2021): 2010329.

[4] Sarkar, Sumant, Ryan O. Behunin, and John G. Gibbs, *Nano letters* 19.11 (2019): 8089-8096.

EL-TuP-4 A Review of Refractive Index Refinements Analysis in Mono layers Absorbents Atomic Layer Deposition (ALD) or Molecular Physisorption Phenomena, *F. Ferrieu,* Optical Polarimetry Ellipsometry, Switzerland; ***Christophe Vallee***, SUNY POLY, Albany

In situ Spectroscopic Ellipsometers (SE), is a precious real time process control tool. As frequently reported in literature, very thin layers measurements don't yield however simultaneous and uncorrelated values for the thickness t_F and the material refractive index (ri). Thickness values are highly related with the choice of an a priori assumed ri which a characteristic of the intrinsic layer's nature. The paper implements an earlier analysis of the initial Drude equations. We show that when thickness turns ultra-thin thenthe ellipsometry equations can be solved through a first order expansion in t_F. During growth, deposition or in thecase of physical adsorption on a substrate, this hypothesis is entirely fulfilled. After describing the simple way to proceed data, within Atomic Layer Deposition (ALD) examples, it is shown how few physi-sorbed monolayerscase can be handled so far. More general molecular physisorption is also considered. Particularly in theCO_2/H_2O gas adsorption inter exchange, ellipsometry turns a right method with absorbent like thin or nativesub-oxide samples. Both refractive index and thickness with high accuracy are independently reachable andwithin a rather fast acquisition capability. This will be shown in this poster.

Moreover, in vacuum chambers, the stability of alignment is just being done one time and fully optimized. A fixed physicalconfiguration inside vacuum chambers acts with benefit over usual limiting factors. An evident interest appearsin atomic layer deposition or etching as well for molecular beam epitaxy and chemical vapor depositionstechniques, and sputtering. With today's "no moving part" or "one single shot" photonic technologies,Spectroscopic Ellipsometers within this configuration can provide sensitivity more than Surface PlasmonResonance SPR which measures only the optical thickness. With the use of a limited number of wavelengths,SE exist in wide applications fields and furthermore depolarization factor acquisition gives an additionalinformation on the player building accomplishment. Since the pioneer works from H. Arwin, a large opening forbio photonics sensors appears also today. Thin silica interacting with ambient is recognized as specific adsorbents material for gases and proteins detection which is observed here in "native" oxides layers.

Electronic Materials and Photonics Division
Room 304 - Session EM+AS+EL+NS+SS-ThA

Interfaces and Defect Engineering in Electronic & Photonic Materials & Devices

Moderator: Erin Cleveland, U.S. Naval Research Laboratory

2:20pm **EM+AS+EL+NS+SS-ThA-1 Design and Control of Defect-Mediated Properties in Electronic Ceramics*, Elizabeth Dickey,*** Carnegie Mellon University **INVITED**

Crystalline lattice defects, e.g. vacancies, interstitials or substitutional ions, play an important role in the conductivity and dielectric properties of electronic ceramics. The material "defect chemistry" can be tuned to optimize the electronic and ionic conductivities for particular applications via doping, oxygen-activity and temperature control during processing. Beyond controlling the majority defect (carrier) concentrations, it is also important to control the minority defect concentrations as these can be especially relevant to the time-dependent electrical behavior. For example, applied electric fields in device applications provide a strong driving force for the electromigration of charged lattice defects. Furthermore, external conditions such as humidity, which can lead to proton incorporation, can also strongly influence time-dependent material properties. This talk will review our current understanding and implications of point defect equilibria, partial equilibria and dynamics in several prototypical electronic ceramics. Recent efforts to effectively co-dope dielectric materials to improve simultaneously limit both the electronic and ionic conductivity will be discussed.

3:00pm **EM+AS+EL+NS+SS-ThA-3 In-Situ Investigation of the Interface Formation between Si-Terminated Diamond and a NbxOy Electron Acceptor Layer for Electronic Applications*, Gabrielle Abad,*** *P. Hopkins, S. McDonnell,* University of Virginia

Ultra-wide band gap semiconductors present one avenue for the next generation of semiconductor devices. Diamond, specifically, has shown promise in high power, frequency, and temperature electronics; however, issues with impurity doping has limited the development of diamond-based devices. Instead, surface charge transfer doping (SCTD), which avoids introduction of foreign atoms into the diamond lattice, has been used for inducing a two-dimensional hole gas at the diamond surface thus increasing its conductivity. The established method to achieve SCTD is to hydrogen-terminate the diamond surface prior to the addition of an electron acceptor layer; however, the degree of SCTD induced by H-termination is largely dependent on atmospheric exposure. Alternatively, silicon-termination of the diamond surface has been shown to produce the ordered surface with the negative electron affinity necessary for the SCTD mechanism. In this work, we investigate the combination of Si-terminated diamond with a Nb_xO_y electron acceptor layer, wherein we focus on understanding interface formation and chemistries, as well as elucidating if the band alignment mechanism is responsible for SCTD for this material system. Ultra-high vacuum (UHV) electron beam (e-beam) deposition of Si onto diamond substrates was carried out, followed by UHV annealing to produce the Si-terminated (100) diamond surface. X-ray photoemission spectroscopy (XPS) of core-level and valence band spectra was used to analyze chemical composition. To form the electron acceptor layer, Nb films were e-beam deposited onto the Si-terminated diamond surface by depositing Nb under varying oxygen partial pressures. XPS was used to observe how interfacial chemistry, electronic structure, and band alignment evolve with different Nb_xO_y compositions. The air stability of the electron acceptor layers was also investigated after atmospheric exposure via XPS. Analysis of the valence band spectra shows that band alignment would not result in SCTD for the Nb_xO_y/Si/diamond material system.

3:20pm **EM+AS+EL+NS+SS-ThA-4 Effects of Atmospheric UV-O_3 Exposure of WSe_2 on the Properties of the HfO_2/WSe_2 Interface*, Maria Gabriela Sales,*** University of Virginia*; A. Mazzoni,* University of Maryland College Park*; W. Sarney,* Army Research Laboratory*; J. Pearson,* University of Maryland College Park*; S. Najmaei,* Army Research Laboratory*; S. McDonnell,* University of Virginia

Transition metal dichalcogenides (TMDCs) are a class of two-dimensional (2D) layered materials, in which each layer is held in-plane by strong chemical bonds, but held in the out-of-plane direction by weak van der Waals forces. For integration in an electronic device, TMDCs are typically capped in the gate region with a high-quality dielectric layer, where ultrathin (sub-5 nm) dielectric thicknesses are desired in order to achieve sufficient gate to channel electrostatic coupling. The unreactive basal plane of TMDCs makes atomic layer deposition (ALD) of dielectric films directly on top of these 2D materials challenging. In this work, we investigate the effects of atmospheric ultraviolet-ozone (UV-O_3) exposures of WSe_2 and use the UV-O_3 functionalized WSe_2 surfaces as substrates for ALD of HfO_2. We report two UV-O_3 functionalization regimes observed on WSe_2: lower exposure times, which do not result in oxidation of the WSe_2 surface, and higher exposure times, which result in a tungsten oxyselenide top layer. The properties of this oxidized layer, such as its thickness, structure, air stability, and thermal stability, are also investigated. Additionally, we note that both functionalization regimes result in variably doped WSe_2. We report on the interface chemistry observed after subsequent ALD of HfO_2, as measured with X-ray photoelectron spectroscopy (XPS). We note that variable, depth-sensitive doping states are found in the WSe_2 functionalized with higher exposure times. We also study the resultant morphologies of our deposited HfO_2 films with atomic force microscopy (AFM), and we find that both of our UV-O_3 functionalization regimes result in uniform and smooth HfO_2 films directly deposited by ALD. With the different functionalization regimes (with different interface chemistries) all providing uniform dielectric film deposition, our atmospheric UV-O_3 exposure technique on WSe_2 presents unique tunability and flexibility in the design of interfaces in devices.

3:40pm **EM+AS+EL+NS+SS-ThA-5 Near Zero Field Magnetoresistance and Electrically Detected Magnetic Resonance Studies of Instabilities in Semiconductor/ Insulator Systems*, Patrick Lenahan,*** Pennsylvania State University **INVITED**

We have utilized both electrically detected magnetic resonance(EDMR) and near zero field magnetoresistance (NZFMR) spectroscopy to investigate the physics involved in instabilities such as stress induced leakage currents and time dependent dielectric breakdown in Si/SiO_2 and SiC/ SiO_2 systems. Both techniques are extremely sensitive and extend the sensitivity of conventional electron spin based techniques down to near nanoscale device structures. We find that the very simple spin-based NZFMR technique has significant analytical power in these investigations. The NZFMR studies can complement the more established EDMR measurements with simple and relatively inexpensive apparatus.

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