Monday Morning, November 6, 2023

Spectroscopic Ellipsometry Technical Group
Room C124 - Session EL1-MoM

Big Data, AI and Analytical Methods

Moderators: David Aspnes, North Carolina State University, **Tino Hofmann**, University of North Carolina at Charlotte

8:20am **EL1-MoM-1 Ellipsometry Analysis Overview: Things We Can't Ignore***, **Nikolas Podraza**, A. Bordovalos,* University of Toledo*; P. Dulal, N. Jayswal, M. Mainali, E. Miller, B. Shrestha, M. Tumusange, R. Collins, A. Shan,* University of Toledo, United States Minor Outlying Islands (the) **INVITED**

Most spectroscopic ellipsometry measurements are relatively straightforward to make (but still must be done with care), however the analyses may not be straightforward even for seemingly simple samples.Appropriate and justifiable structural and optical property models must be developed to obtain meaningful information from measured ellipsometric spectra.However, even after substantial time spent analyzing data all of us in the field ask:"Is this the correct model?"More complicated measurement configurations and simultaneous analysis of multiple sets of spectra can either help answer that question or make the situation even more challenging and uncertain.A follow up question also becomes "When do I stop?"Many of us have also spent long amounts of time (sometimes far more time than we should in retrospect) trying to describe small, nuanced features in our measured spectra that we simply can't ignore.To answer those questions, there are also things we can't ignore in the analyses of ellipsometric spectra including if the structural model makes sense; if the complex optical properties obtained are Kramers-Kronig consistent and appropriate for the type of material and spectral range measured; the extent of surface or interfacial layer effects and our ability to describe them meaningfully; and of course the parameters of interest to be extracted from our models, quality of fit, confidence limits, and correlation matrices.These considerations will be discussed for metallic, semiconducting, and dielectric thin film and bulk materials characterized by spectroscopic ellipsometry spanning the ultraviolet (UV) to terahertz (THz) range.This will include strategies for analyzing thin films with unknown optical properties, samples with complicated structures (and knowing when to stop), mapping spectroscopic ellipsometry data, and in situ real time spectroscopic ellipsometry data.Most examples we will discuss are materials used in thin film polycrystalline solar cells based on hybrid organic inorganic lead halide based perovskites, cadmium telluride, and copper indium gallium diselenide absorbers as well as spectroscopic ellipsometry characterization of complete, functional solar cells.

9:00am **EL1-MoM-3 Noise Reduction Using Linear and Nonlinear Filtering***, **Long V. Le**,* Institute of Materials Science, Vietnam Academy of Science and Technology, Viet Nam **INVITED**

If lineshape distortion and loss of information are not factors, linear low-pass filters are very effective at eliminating noise from spectra. However, achieving the balance among lost information, leaked noise, and Gibbs oscillations (ringing) can be difficult. Many linear filters are available that operate with direct-(spectral) space (DS) convolution. This approach is convenient, and endpoint discontinuities in value or slope have only local effects. However, intelligent linear filtering requires assessments in reciprocal-(Fourier) space (RS), capitalizing on the separation of information and noise into low- and high-index Fourier coefficients, respectively. Comparing the information content of the data to the RS transfer function of the filter is necessary if filtering is to be performed intelligently.

We recently quantified the tradeoff between reducing noise and preserving information by capitalizing on Parseval's Theorem to cast two DS measures of performance, mean-square error (MSE) and noise, into RS. This provides quantitative insight not only into the effectiveness of the various linear filters but also information on how they can be improved. The best practical linear filter was found to be the Gauss-Hermite filter introduced about 20 years ago by Hofmann and co-workers.

Nonlinear filters have an interesting history, which is reviewed briefly. Originally designed to "whiten" (sharpen) structure in spectra, a recent solution of Burg's equations allows the trend established by low-index Fourier coefficients to be extrapolated into the white-noise region in a model-independent way. This corrected-maximum-entropy (CME) filter achieves all 3 goals: information is left intact, noise is eliminated, and by eliminating apodization, ringing is also eliminated. Recent progress includes adapting the theory to filter general lineshapes. By introducing an enhancement factor in the ME equations, weak features can be discovered and structures enhanced without the complications inherent in Burg's original result. Examples will be provided throughout, along with MATLAB programs that perform the processes discussed.

9:40am **EL1-MoM-5 Numerical Ellipsometry: Artificial Intelligence Methods for Solving Ellipsometer Data***, **Frank Urban**, D. Barton,* Florida International University

Ellipsometry is a material analytical method which works by measuring the change in polarization state of light reflecting from or transmitting through the material of interest.Desired parameters, such as thin film thickness and optical properties, are related by mathematical models to the measurements themselves. In the beginning those parameters were obtained by lookup using a printed table provided along with a commercial ellipsometer.This was followed by solution methods using a calculator and this evolved to the personal computer based programs that are in use today.Because a single ellipsometer measurement provides two real numbers, typically Ψ and Δ, it can provide for determination of only two unknowns associated with the reflecting surface regardless of whether other measurement modes are employed such as Mueller matrix forms.As a consequence it usually became necessary to make use of more than a single measurement at a single wavelength to obtain more than two parameters.Two of the ways forward are to take multiple measurements at each wavelength of interest to obtain data sufficiency and the other way is to take spectroscopic measurements with the aim of solving for optical constants as represented as various functions (fitting functions) of wavelength.For the spectroscopic approach the match to the Maxwell equations and to the selected "fitting functions" by which the number of unknowns is reduced hugely by the small number typically three or four per fitting function.Thus data sufficiency is achieved at the cost of requiring good selections of fitting functions which might not be unique.We have found, following earlier work, that current Artificial Intelligence methods in the form of Deep Learning or Artificial Neural Networks offers a new way to obtain solutions or at least to provide very accurate initial estimates from which numerical method solutions can reliably and accurately be determined.The work presented here both covers a two measurement method AI network at single wavelengths and spectroscopic measurements (a thousand or more) using fitting functions.Accuracy, speed, and ease of use will be demonstrated.

10:00am **EL1-MoM-6 Modeling Many-body Effects in Ge Using Pump-Probe Time-Resolved Spectroscopic Ellipsometry***, **Carlos A. Armenta**,* New Mexico State University*; M. Zahradnik, M. Rebarz,* ELI Beamlines Facility, The Extreme Light Infrastructure ERIC, Czechia*; S. Espinoza,* ELI Beamlines Facility, The Extreme Light Infrastructure ERIC*; S. Vazquez-Miranda,* ELI Beamlines Facility, The Extreme Light Infrastructure ERIC, Czechia*; J. Andreasson,* ELI Beamlines Facility, The Extreme Light Infrastructure ERIC*; S. Zollner,* New Mexico State University

We analyze the transient dielectric function (TDF) of Ge at very high electron-hole pair densities via time-resolved spectroscopic ellipsometry. Through a pump-probe technique, the bulk Ge is photoexcited up to densities of around $\sim 3\times10^{21}$ cm^{-3}. We specifically focus on the E_1 and $E_1+\Delta_1$ critical points and how their parameters such as energy and broadening change as a function of delay time.

Our analysis aims to model the TDF of Ge and describe its behavior at different carrier concentrations. In particular, it addresses phase-filling singularities that are usually difficult to study in implanted and annealed samples due to defects. High-power laser induced carriers can achieve density levels on undoped samples that are ideal for the study of many-body phenomena. The model also addresses other effects taking place during the excitation and relaxation of electrons, such as excitonic screening and acoustic phonon oscillations produced by the transferring of energy to the lattice.

Spectroscopic Ellipsometry Technical Group
Room C124 - Session EL2-MoM

Industrial Applications of Spectroscopic Ellipsometry

Moderators: Andy Antonelli, Nanometrics, **Stefan Zollner**, New Mexico State University

10:40am **EL2-MoM-8 Spectroscopic Ellipsometry and Reflectometry for Advanced Semiconductor Metrology*, Shankar Krishnan,*** KLA Corporation **INVITED**

This presentation will provide an overview of Spectroscopic Ellipsometry (SE) and Spectroscopic Reflectometry (SR) and how they enable KLA to provide advanced metrology solutions in the semiconductor industry.It will focus on both Film and Critical Dimension (CD) Metrology and provide an in-depth look into the latest hardware, algorithms and selected applications in Logic/Foundry and Flash/DRAM.Key hardware innovations including simultaneous multi-AOI ellipsometry, Vacuum Ultraviolet (VUV) – Infrared (IR) broadband ellipsometry, small-spot and ultra-high resolution optical designs will be discussed.We will show how a multi-Angle-of-incidence (AOI) SE contains unique spectral signatures in each AOI and in selected Mueller matrix elements to enable detailed measurements in shape and profiles in the Gate-All-Around (GAA) structures.We will demonstrate how a high-resolution optical system and a combined SE+SR signal are needed in order to be sensitive to changes within small regions (zones) of a 3D-NAND film stack.The value of Deep UV/VUV photons and the enhanced sensitivity to film thickness and film composition of high-K dielectric and threshold voltage layers will be described.This presentation will also touch on the use of SE/SR to measure emerging applications involving very large-pitch structures and on transparent substrates and waveguides.Lastly we will also present a summary of recent advances in algorithms using model-based and model-assisted machine learning to solve critical metrology problems like GAA, hybrid bonding and focus-dose measurements.

11:20am **EL2-MoM-10 Ellipsometry in Industrial Applications*, Andre Miller,*** Intel **INVITED**

Optical Critical Dimension (OCD) metrology, the use of spectroscopic ellipsometry on patterned structures, is the dominant inline shape metrology technique in the semiconductor industry. The technique is used to output geometric parameters for the device patterns on the wafer. This information is used to control the line, to determine processing conditions at subsequent steps and to establish correlations to predict and improve performance and yield. The primary limitations are internal model parameter correlations and requirement for a periodic structure that may not accurately represent the structures of the device.

Nanoscale Science and Technology Division
Room B113 - Session NS2+2D+BI+EL+SS-MoM

Chemical Identification with Scanning Probe Microscopy

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Harald Plank**, Graz University of Technology

10:40am **NS2+2D+BI+EL+SS-MoM-8 Nanoscale imaging with photo-induced force microscopy*, Eric Potma,*** University of California Irvine **INVITED**

Imaging with molecular contrast at the nanoscale is important for a myriad of applications, yet it remains a technical challenge. Over the past two decades, various flavors of optical spectroscopy combined with atomic force microscopy have been developed, each offering hope for a more routine nanospectroscopy technology. One of these approaches is photo-induced force microscopy (PiFM), a non-contact scan probe technique that is sensitive to the light-induced polarization in the material. PiFM has been used to generate molecular maps with 5 nm resolution, based on absorption contrast or on contrast derived from nonlinear optical interactions. Nonetheless, questions remain about the origin of the signal, in particular the possible contribution of forces that result from the thermal expansion of the sample. In this presentation, we will discuss various physical mechanisms that contribute to the PiFM signal and highlight several applications that are unique to the PiFM technique.

11:20am **NS2+2D+BI+EL+SS-MoM-10 Near-field Optical Microscopy Imaging and Spectroscopy at 10nm Spatial Resolution*, Artem Danilov,*** Attocube Systems Inc.

Fourier-transform infrared (FTIR) spectroscopy is an established technique for characterization and recognition of inorganic, organic and biological materials by their far-field absorption spectra in the infrared fingerprint region. However, due to the diffraction limit conventional FTIR spectroscopy is unsuitable for measurements with nanoscale spatial resolution. Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) allows to overcome the diffraction limit of conventional light microscopy or spectroscopy enabling optical measurements at a spatial resolution of 10nm, not only at IR frequencies but also in the whole spectral range from visible to terahertz. s-SNOM employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample and detection of the elastically tip-scattered light yields nanoscale resolved near-field images simultaneous to topography.Use of material-selective frequencies in the mid-IR spectral range can be exploited to fully characterize polymer blends or phase change polymers with nanometer-scale domains. Quantification of free-carrier concentration and carrier mobility in doped semiconductor nanowires, analysis of 2D (graphene) nanostructures, or study phase propagation mechanisms in energy storage materials is achieved by amplitude- and phase-resolved near-field imaging. Furthermore, here we introduce correlative tip-enhanced nanoscopy, enables complete collocal vibrational analysis of both IR- and Raman-active modes at the same spatial scale. Our instrument allows for a straight-forward implementation of nano-PL measurements using background suppressing provided by the demodulation of detector signal utilized in nano-FTIR detection scheme. Combining Raman, TERS, nano-FTIR and nano-PL measurements in the same instrument significantly reduces the effort of correlating the resulting datasets, enabling complete optical analysis at nanoscale, which has not been possible so far.

11:40am **NS2+2D+BI+EL+SS-MoM-11 Correlative Nanoscale Chemical, Mechanical and Electrical Property Mapping on a Single AFM-IR Platform***, C. Li,* ***Martin Wagner****, C. Phillips,* Bruker Nano Surfaces Division

Chemical identification on the nanoscale is a long sought after capability from the inception of AFM. AFM-IR has proven to be uniquely successful in achieving this among all other attempts. It uses a mid-IR laser that is focused onto the AFM tip. Light absorption by the sample results in photothermal expansion that causes a detectable cantilever deflection change of the AFM probe. The obtained IR spectra correlate with conventional FTIR spectroscopy but are associated with sub-10nm spatial resolution.

However, a single data set rarely tells the full story and multiplexed analysis is essential to fully understand a material. We use an AFM-IR microscope with image registration and overlay capability to return to the same position on a sample when changing AFM probes, enabling extensive multimodal analysis. Data on a two-component polymer sample PS-LDPE comprising polystyrene and polyethylene reveals nanoIR spectra that correlate well with FTIR, while nanoIR maps at different IR wavenumbers provide the spatial distribution of each component. Further, we show that they are directly correlated at the nanometer level through PeakForce QNM elastic modulus and adhesion maps, as well as work function (surface potential) and dielectric maps with FM-KPFM (frequency-modulated Kelvin probe force microscopy). Many of the properties can be conveniently obtained simultaneously, while others are preferably obtained sequentially in a colocalized manner with the optimal probe choice and parameter settings for each AFM mode. Data on real-world industrial samples is then discussed, e.g. SBR (styrene-butadiene rubber) with carbon-black additives for car tires, exemplifying how ratio-map and multimodal property mapping unravel information not seen through one technique alone. In another use case chemical identification is complemented by nDMA, a mode where viscoelastic nanoscale sample properties are measured that match bulk dynamic mechanical analysis (DMA) data.

Spectroscopic Ellipsometry Technical Group
Room C124 - Session EL1+TF-MoA

Thin Films & Novel Materials

Moderators: Mathias Schubert, University of Nebraska - Lincoln, **Megan Stokey**, Milwaukee School of Engineering

1:40pm **EL1+TF-MoA-1 Enhancement of Electron Effective Mass in Semiconductor Materials and 2DEGs Revealed by THz Optical Hall Effect**, ***Nerijus Armakavicius,*** Linköping University, Sweden*; S. Knight,* Linköping University*; P. Kuhne, H. Zhang, R. Carrascon,* Linköping University, Sweden*; S. Richter,* Linköping University, Lund University, Sweden*; V. Stanishev,* Linköping University, Sweden*; M. Schubert,* Linköping University, Sweden, University of Nebraska-Lincoln*; P. Paskov,* Linköping University, Sweden*; V. Darakchieva,* Lund University, Sweden **INVITED**

Progress in semiconductor material technology continues to enable significant advances in nearly all scientific endeavors and lies at the heart of modern information and communication networks. Wide band gap semiconductors, such as GaN and SiC transpire as key materials to address the demands of next-generation quantum technology and green electronics.Understanding transport in semiconductor materials is a prerequisite for their implementation in advanced device architectures with improved functionalities. Electron effective mass is a fundamental material parameter defining the free charge carrier transport but it is very challenging to be directly determined at high temperatures and frequencies relevant for device operation.

With the advent of the optical Hall effect (OHE), which consists of performing generalized spectroscopic ellipsometry at long wavelengths in magnetic field the determination of the electron effective mass tensor at variable temperatures has became possible without the need to invoke any additional electrical measurements [1,2]. The OHE describes the external magnetic field induced anisotropic charge displacement in materials when interacting with electromagnetic waves and allows for the determination of the charge carrier sign, concentration, mobility and effective mass parameters [2].

In this work, we present a comprehensive investigations of the electron effective mass parameters in GaN bulk and epitaxial layers, as well as in two-dimensional electron gas (2DEG) in GaN based high-electron mobility transistor structures [3,4] by THz and MIR OHE [5]. OHE analysis allows to extract the free charge carrier concentration and mobility in the various structures as a function of temperature and the results are found to be in a good agreement with the respective parameters obtained by electrical Hall effect and capacitance-voltage measurements. In addition, the electron effective mass parameter is determined from the OHE at temperatures from 10K to 370K. At low temperatures (< 100 K) an electron effective mass of approximately $0.20m_0$ is obtained in agreement with the well accepted value. Unusual enhancement of the electron effective mass is discovered with increasing temperatures to room temperature and above for both bulk, epitaxial and 2DEG GaN systems. We evaluate and discuss various mechanisms such as band gap nonporabolicity, magnetic field, strain and polaron effects,that could potentially contribute to the observed increase. We propose a frequency-dependentscattering time to be at the origin of the effective mass enhancement. We also discuss possible deviations of the free electron behavior from the classical Drude model and its implications for transport and devices operating at high temperatures (room temperature and above) and frequencies (100 GHz to 1THz).

References

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[2] M. Schubert et al., J. Opt. Soc. Am. A 33, 1553 (2016).

[3] A. Papamichail et al., Appl. Phys. Lett. 122, 153501 (2023).

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[5] P. Kühne et al., IEEE Trans. Terahertz Sci. Technol. 8, 257 (2018).

2:20pm **EL1+TF-MoA-3 In Situ and Real Time Spectroscopic Ellipsometry of Polycrystalline $CuInSe_2$ Co-Evaporation for Narrow Bandgap Photovoltaic Absorbers***, D. Sapkota,* ***Balaji Ramanujam****, M. Alaani, A. Shan, N. Podraza, R. Collins,* University of Toledo

Deposition processes for narrow bandgap (E_g = 1.02 eV) polycrystalline $CuInSe_2$ (CIS) thin films with intended applications as photovoltaic (PV) absorbers have been developed and studied using various techniques of in situ and real time spectroscopic ellipsometry (SE). Real time SE analyses of two series of sequentially deposited Cu and In_2Se_3 thin films on the same substrates, but at different Cu and In evaporation source temperatures, serves as an accurate source calibration method. This calibration enables co-evaporation of CIS films at independently controllable deposition rates and compositions, the latter characterized by the [Cu]/[In] molar ratio which establishes their p-type character as PV absorbers. In situ SE analyses of the starting crystalline Si substrates provide an accurate substrate temperature calibration, and real time SE of CIS co-evaporation on such substrates provides insights into polycrystalline nucleation and grain coarsening processes. In contrast to earlier studies of hydrogenated amorphous silicon PV absorbers, the highest device quality CIS absorbers are obtained in processes leading to the most extensive increases in the surface roughness layer thickness with bulk layer thickness, characteristic of crystallites of increasing size protruding from the film surface. Real time SE provides the time evolution of the surface roughness layer, bulk layer, and effective thicknesses for the deposited film, where the effective thickness is the volume per planar area of substrate and, thus, includes the surface roughness contribution. The effective thickness is used to evaluate the deposition rate for the desirable situation in which the roughness thickness increases continuously with bulk layer thickness. For substrate temperatures of 500°C and below in CIS co-evaporation, the roughness thickness is relatively stable with increasing bulk layer thickness at values controlled by the initial nucleation. At higher temperatures, in contrast, the surface roughness thickness increases rapidly and continuously with bulk layer thickness, well above that observed in the initial nucleation process. Such grain growth enhancement is also reflected in the following variations in the final film properties with increasing substrate temperature: (i) an increased grain size as determined by the widths of the peaks in the X-ray diffraction pattern, (ii) a reduction in the bandgap critical point broadening parameter from ex situ SE, consistent with an increase in the grain boundary scattering time for excited carriers, (iii) a steeping of the Urbach tail, and (iii) higher performance PV devices for absorbers incorporated into cell structures.

2:40pm **EL1+TF-MoA-4 Anisotropic Optical Properties of $GdScO_3$***,* ***Prabin Dulal****, E. Miller,* University of Toledo*; D. Sotir, M. Barone, D. Schlom,* Cornell University*; N. Podraza,* University of Toledo

$GdScO_3$ is a wide-band gap semiconductor with a high dielectric constant, the potential to replace SiO_2 in silicon-based transistors, and use as a substrate for epitaxial thin film growth. It has an orthorhombic crystal structure resulting in crystallographic and optical anisotropy. The optical properties in the form of complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra for each principal direction of single crystal $GdScO_3$ are investigated using generalized spectroscopic ellipsometric spectra collected over the photon energy range from 0.70 to 8.50 eV. Multiple sets of generalized ellipsometric spectra are collected from (001) and (110) surface plane oriented single crystals of $GdScO_3$ as a function of rotation about the surface normal. A divided spectral range analysis is used to determine the structural parameters of the $GdScO_3$ including bulk and surface layer thicknesses and the azimuthal Euler angle for each measurement while the remaining Euler angles are fixed based on known lattice parameters and the respective surface plane cut. In divided spectral range analysis, the full measured spectra range is subdivided into nominally transparent, weakly absorbing, and highly absorbing regions. A common structural model is used to describe the transparent and the highly absorbing spectral region to obtain common structural parameters while separate physically realistic models are applied to describe spectra in ε in each direction and both of these spectral regions. The weakly absorbing region is initially ignored as the line shape describing ε is not initially known. After obtaining structural parameters, numerical inversion is then used to extract ε corresponding to electric fields oscillating parallel to each crystallographic axis over the full spectral range, including the initially ignored weakly absorbing region. Critical points transition in *ε* corresponding to each direction are identified by simultaneously fitting each numerically inverted spectra in ε_2 and $d\varepsilon_2/dE$ using a sum of critical point parabolic band (CPPB) oscillators. A piecewise parameterization is developed that includes an Urbach tail below the band gap energy and CPPB behavior at and above the band gap energy to parameterize the numerically inverted optical response. The lowest direct transition is identified at 6.46 eV for electric fields oscillating parallel to a-axis, and above gap critical transitions at 6.72, 6.78, 6.95, 7.40, 7.92, and 8.25 eV are identified from all spectra in ε.

3:00pm **EL1+TF-MoA-5 Combined Density Functional Theory and Spectroscopic Ellipsometry Studies of Anisotropic Materials**, ***Rafal Korlacki**, M. Hilfiker, M. Stokey, M. Schubert,* University of Nebraska-Lincoln **INVITED**

The ability of spectroscopic ellipsometry (SE) to resolve all components of the dielectric tensor combined with the predictive power of density functional theory (DFT) and related first-principles methods, is a particularly useful combination of techniques to study anisotropic materials. In recent years, a wide-bandgap gallium oxide Ga_2O_3 is a promising candidate for applications in high-power electronic devices. The most stable *β* phase, which can be grown as a high-quality bulk crystal is highly anisotropic, thanks to the low-symmetry monoclinic lattice [1,2]. In order to further increase the bandgap, the alloys of gallium oxide and aluminum oxide, $(Al_xGa_{1-x})_2O_3$, can be epitaxially grown on gallium oxide substrates. Heteroepitaxial films are inherently strained. The dependence of material properties on the components of the strain tensor for monoclinic crystals have been obtained from symmetry analysis [3], and the linear deformation potentials for energies of phonon modes and band to band transitions in Ga_2O_3 - from DFT calculations [3,4]. The same principle can be applied to the monoclinic phase of Al_2O_3, and Vegard's rule can then be used to construct a simple universal model of strain and composition dependencies of various material properties, including band-to-band transitions, refractive indices, components of the dielectric tensors, and effective mass parameters. Thus, these dependencies can be fully resolved for actual heterostructures under specific strain patterns [5,6].

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Spectroscopic Ellipsometry Technical Group
Room C124 - Session EL2-MoA

Instrumentation

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Nikolas Podraza**, University of Toledo

4:00pm **EL2-MoA-8 Advancing Metrology in Semiconductor Manufacturing: Challenges and Novel Ellipsometry Techniques**, *M. Lee, **Wookrae Kim**,* Samsung Electronics Co., Inc., Republic of Korea **INVITED**

Manufacturers of semiconductor devices must ensure uniformity in the critical dimension (CD) for proper device functionality. Precision and accuracy in semiconductor metrology and inspection are crucial to accurately measure even the smallest details of semiconductor structures. Minor imperfections in the CDs can result in device malfunctions, highlighting the importance of maintaining high levels of precision.

Ellipsometry has been a powerful method used in high volume manufacturing to provide 3D information on sample structures and achieve high measurement throughput. However, the continuous evolution of semiconductor devices with new designs, high aspect ratio contacts, and smaller cell sizes has given rise to new metrology requirements, presenting various technical challenges. As a result, further advancements in standard ellipsometry techniques are needed to meet these requirements and overcome the challenges they pose.

There are several specific challenges that need to be addressed. Firstly, the decreasing cell size in DRAM and SRAM makes smaller metrology spot sizes critically important. Secondly, the required metrology sensitivity and precision specifications become more stringent in high volume manufacturing (HVM). In the case of VNAND devices, the new cell-on-peri architecture restricts the use of the full wavelength of light from the tool, and the increasing aspect ratio of contacts limits the application of critical angle illumination in spectroscopic ellipsometry. Additionally, the number of measurement points on a wafer increases exponentially for advanced devices, necessitating innovative solutions to enable massive measurements. Finally, the time required to develop regression models is a significant drawback, particularly during the research and development (R&D) period.

To overcome these challenges, researchers have been developing various innovative techniques. These include high throughput imaging ellipsometry for massive measurements, highly sensitive pupil ellipsometry, infrared (IR) ellipsometry, and small spot ellipsometry, among others. I will present an overview of the challenges faced by ellipsometry techniques in semiconductor manufacturing and review the recently introduced novel ellipsometry techniques.

4:40pm **EL2-MoA-10 Mid-Infrared Ellipsometry for High Aspect Ratio Semiconductor Process Control Applications**, ***Troy Ribaudo**,* Onto Innovation **INVITED**

Optical critical dimension metrology (OCD) has been a critical process control tool in the semiconductor industry for many years. Traditional OCD measurement platforms operate within the ultraviolet to near infrared spectral range and combine Mueller Matrix spectroscopic ellipsometry spectra with RCWA simulations of complex 3-dimensional models to effectively measure subwavelength geometrical properties. In recent years, challenges regarding sensitivity and parameter correlation performance metrics have reduced the efficacy of the technique, specifically for some key VNAND technology applications with high aspect ratio structures. This situation has been remedied through the development of a spectroscopic ellipsometer which operates in the mid-infrared part of the electromagnetic spectrum. In both the lab and the field, it has been proven to outperform the existing OCD technologies for a number of those important applications.

In this talk, we shall describe the theoretical considerations that led to the change of spectral range on this unique OCD platform. We will also show a performance comparison of the two classes of OCD systems on the already explored high aspect ratio applications as well as simulations showing performance estimates as VNAND technology continues to evolve.Finally, a description of the technology roadmap for the product line will be described.

Spectroscopic Ellipsometry Technical Group
Room Oregon Ballroom 203-204 - Session EL-TuP
Spectroscopic Ellipsometry Poster Session

EL-TuP-1 Dielectric Function of Tantalum Nitride Formed by Atomic Layer Deposition on 300 mm Wafers*, Aaron Lopez Gonzalez*, *Y. Hettige, J. Love, S. Zollner,* New Mexico State University*; E. Bhatia, T. Vo, S. Papa Rao,* NY CREATES

In this undergraduate student poster, we describe the dielectric function of atomic layer deposition (ALD) tantalum nitride (TaN) from 0.03 eV to 6.6 eV determined from spectroscopic ellipsometry.

First, thermal oxides with about 50 nm thickness were grown on B-doped 10 Ωcm Si (100) 300 mm diameter wafers. Tantalum nitride layers with 12 nm and 25 nm thickness were then formed by atomic layer deposition using 300 mm process tools. The TaN layer thicknesses were confirmed by x-ray reflectance (XRR). The TaN surface roughness (also derived from XRR) was on the order of 0.5 nm. On a vertical J.A. Woollam variable angle of incidence rotating-analyzer ellipsometer (V-VASE), the ellipsometric angles ψand Δ were acquired at room temperature at incidence angles from 50° to 80° and photon energies from 0.5 to 6.6 eV with 0.02 eV steps. We used a Berek wave plate compensator and measured with both positive and negative polarizer angles to improve accuracy. We selected a broad range of incidence angles, because the Brewster angle of SiO_2 (55°) is much smaller than that of Si (75°). We also acquired the infrared ellipsometric spectra at the same angles of incidence from 0.03 to 0.70 eV with 8 cm^{-1} resolution on a J.A. Woollam Fourier-transform infrared ellipsometer.

We first developed an ellipsometry model for the optical constants of the thermal oxide, using three Gaussian oscillators at 56, 132, and 146 meV in the infrared spectral region to describe the silicon-oxygen vibrations and a pole at 11 eV (fixed) with variable amplitude to model the visible and ultraviolet dispersion. The TaN layers were described with a Tauc-Lorentz oscillator centered at 3.2 eV with a band gap at 1.7 eV, one UV pole, and one Gaussian in the UV. The fit could be improved with an infrared Gaussian between 0.7 and 1.1 eV, but this peak could be an artifact arising from the uncertainty of the precise layer thicknesses. Across wafer uniformity of the band gap was determined for both thicknesses by performing spectroscopic ellipsometry on coupons from the wafer center, mid radius, and wafer edge. We will perform ellipsometry measurements at low temperatures to investigate the temperature dependence of the optical constants and oscillators.

EL-TuP-2 A Generalized Maximum-Entropy Approach for Eliminating Apodization and Associated Errors in Noise Reduction*, L. V. Le,* Institute of Materials Science, Vietnam Academy of Science and Technology, Viet Nam*; Y. Kim,* Department of Physics, Kyung Hee University, Republic of Korea*; D. Aspnes,* North Carolina State University

In linear filtering, apodization requires compromises to be made among noise leakage, information loss, and Gibbs oscillations (ringing). This problem, inherent in linear filtering, is avoided with the corrected maximum-entropy (CME) procedure. In CME, apodization and associated errors are eliminated by projecting trends established by low-order coefficients into the white-noise region in a model-independent, most-probable way. However, CME cannot be applied to structures that contain an appreciable dispersion-curve component. Capitalizing on Hilbert transforms, we develop a generalized maximum-entropy (GME) approach that can be applied to any lineshape, thereby allowing white noise to be eliminated completely with no deleterious side effects. Endpoint-discontinuity removal and a Hilbert transform can reversibly convert any segment consisting of a Lorentz/dispersion combination into an absorption spectrum, thus allowing any spectrum to be processed by CME. As an added benefit, Hilbert transforms are exact Kramers-Kronig (KK) transforms of these segments, providing new opportunities for analysis in spectroscopy.

EL-TuP-3 Intelligent Linear Filters for Noise Reduction in Spectroscopy*, Young Dong Kim,* Kyung Hee University, Republic of Korea*; L. Le,* Vietnam Academy of Science and Technology, Viet Nam*; D. Aspnes,* North Carolina State University

A linear filter must strike a balance among reducing noise, preserving lineshapes, and minimizing or eliminating ringing. While nonlinear methods offer superior performance, direct- (spectral-) space (DS) convolution is convenient and may be sufficient in many applications. However, optimization requires reciprocal- (Fourier-) space (RS) considerations. This follows because information appears as point-to-point correlations and noise as point-to-point fluctuations, thereby concentrating information and noise in low- and high-order Fourier coefficients, respectively. For optimum performance, the transfer function of any filter must be consistent with the Fourier transform of the spectrum.

Using Parseval's Theorem, we project typical DS performance measures such as mean-square error (MSE) into RS. The resulting expressions are simpler and more informative than their DS counterparts, providing quantitative insight not only into the effectiveness of different linear filters, but also how they can be improved. Surprisingly, the rectangular ("ideal" or "brick wall") filter is found to be nearly optimal, a consequence of its complete elimination of distortion in low-order coefficients. When ringing is taken into account, the best practical filter is the Gauss-Hermite. Capitalizing on the information provided by these calculations, we develop a version that is demonstrably superior to both brick-wall and Gauss-Hermite filters.

EL-TuP-4 Temperature Dependence of the Fine Structure of the NiO Critical Points*, Yoshitha Hettige,* *C. Armenta, J. Love, S. Zollner,* New Mexico State University*; M. Veis,* Charles University, Prague, Czech Republic

Nickel oxide (NiO) is a cubic charge-transfer insulator. Its valence band consists of Ni 3d and O 2p states. The Ni 3d states split into t_{2g} and an e_g bands. The valence band maximum is a hybridized mixture of O 2p and Ni e_g states. The excited e_g^* band is about 4 ev above the eg band. Optical interband transitions from e_g into e_g^* give rise to a strong absorption peak near 4 eV known as the charge transfer gap. The location of the Ni 4s band is not clear.

In addition to the strong charge transfer gap at 4 eV, there are two other features in the optical spectra of NiO. (1) There is a small amount of absorption between 1 and 4 eV (similar to the indirect absorption of Si) in the pseudodielectric function, which cannot be explained with surface roughness. It is possible that this absorption is due to defects, such as excess oxygen. (2) There are several weak peaks between 1.5 and 4.0 eV. They might be due to interatomic transitions between the Ni 3d orbitals. The temperature dependence of these weak peaks (which we call fine structure) is the topic of this abstract.

In this presentation, we will discuss the temperature dependence of the smaller peaks in these spectra and attribute them to features in the band structure of NiO.

EL-TuP-5 Characterization of Hybrid Organic-Inorganic Perovskite Semiconductors and Solar Cells*, Bailey Frye,* *E. Miller, N. Podraza,* University of Toledo

Hybrid organic-inorganic lead-halide based perovskite semiconductors (ABX_3) are absorber layers in high efficiency single junction and tandem thin film solar cells. The ability to modify the bandgap energies over a wide range is required for these applications, with typical components consisting of an organic molecule A-cation such as methylammonium (MA) or formamidinium (FA), metal B-cation such as Pb or Sn, and a halogen X-anion such as I or Br. Spectroscopic ellipsometry is the ideal characterization technique for determining the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra and thickness of these perovskites as thin films or within solar cell device structures. Various oscillator models have been used to describe ε for these direct-gap, polycrystalline semiconductors. Many models may generate an approximate line shape for ε, but unfortunately lack physically meaningful parameters, are not Kramers-Kronig (KK) consistent — and therefore not physically realistic, or require numerical integration of the KK-integral that is often prohibitively time consuming. A KK-consistent parametric model that uses excitonic critical point parabolic band (CPPB) oscillators and an Urbach tail is presented in this work. CPPBs represent the band-to-band transitions of a semiconductor, including the bandgap, while the Urbach tail describes subgap absorption features. $\varepsilon_2$is described by a series of CPPB oscillators with an Urbach tail and then $\varepsilon_1$is determined from the analytic solution to the KK-integral of ε_2. This parametric model is thus KK-consistent with physically meaningful parameters relevant to direct gap crystalline semiconductors and is shown to model experimental ellipsometric spectra and describe the line shape of ε accurately and quicklyfor various compositions of hybrid organic-inorganic lead-based perovskite semiconductors. This model may be of great use for analyses of perovskite semiconductors that require many data sets, such as real time spectroscopic ellipsometry and ellipsometric spatial mapping. Applications of this CPPB and Urbach tail model to the analysis of ε for

polycrystalline $(FASnI_3)_{1-x}(MAPbI_3)_x$, spatial mapping of $FA_{0.8}Cs_{0.2}Pb(I_{0.65}Br_{0.35})_3$ and $FA_{0.8}Cs_{0.2}Pb(I_{0.6}Br_{0.4})_3$ films including those in the partial and full device structures, and through-the-glass ellipsometry of full solar cells containing perovskite absorber layers are presented in this work.

EL-TuP-6 Many-Body Effects in the Mid-Infrared Dielectric Function of InSb from 80 to 800 K, *M. Rivero Arias, C. Armenta,* New Mexico State University*; C. Emminger,* Leipzig University, Germany*; C. Zamarripa,* New Mexico State University*; N. Samarasingha,* Nova Measuring Instruments*; J. Love, S. Yadav,* ***Stefan Zollner***, New Mexico State University

We describe measurements of the mid-infrared dielectric function of bulk InSb near the direct band gap using Fourier-transform infrared spectroscopic ellipsometry from 80 to 800 K in an ultra-high vacuum cryostat. Indium antimonide is the zinc blende compound semiconductor with the smallest direct band gap (E0=0.18 eV at 300 K) due to its heavy elements and the large resulting spin-orbit splitting and Darwin shifts. The band gap is extracted from the dielectric function by fitting with a parametric oscillator model. It decreases from 80 to 450 K following a Bose-Einstein model, then remains constant up to 550 K, and increases again at the highest temperatures. This is explained with a thermal Burstein-Moss shift: The onset of optical absorption increases as electron-hole pairs are thermally excited at the highest temperatures. The intrinsic carrier concentration determined from the Drude tail in the ellipsometry spectra agrees qualitatively with temperature-dependent Hall experiments and calculations based on degenerate Fermi-Dirac statistics.

EL-TuP-8 Film-Side Versus Through-the-Glass Ellipsometry Measurements of Wide Band Gap Perovskites, ***Emily Amonette****, K. Dolia, B. Frye, Y. Yan, Z. Song, N. Podraza,* University of Toledo

Wide band gap $FA_{0.8}Cs_{0.2}Pb(I_{1-x}Br_x)_3$ (x = 0.3, 0.35, 0.4) perovskite thin films are examined via spectroscopic ellipsometry in both the film-side mapping configuration and as part of complete superstrate photovoltaic (PV) devices. Complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra of the perovskite and all layer thicknesses are determined for all measured samples. Film-side measurements are more commonly performed, and it is often assumed that the resulting ε spectra represent a layer in a complete device, but this work examines variations in perovskite ε and associated characteristics such as the band gap and Urbach energies that may only be apparent when considering data from a complete PV device taken in the through-the-glass configuration. Measurements of partial device-like structures consisting of glass superstrate / indium tin oxide / hole transport layer / perovskite reveal spatial variations in band gap energies ranging from 1.77 to >1.80 eV in the case of $FA_{0.8}Cs_{0.2}Pb(I_{0.6}Br_{0.4})_3$ as well as variations in Urbach energies, while those of complete PV devices consisting of the same structure and perovskite composition but completed with the electron transport layer and metal back contact exhibit less spatial variation, where band gap energies vary only between 1.75 to 1.77 eV. This behavior indicates that atmospheric exposure amplifies perovskite material spatial uniformity. Optical property and thickness information from through-the-glass ellipsometry is used to simulate external quantum efficiency (EQE) spectra, and by comparing these simulations to experimental EQE, information about both optical and electronic loss in PV is obtained.These data sets comprised of many similar but slightly different samples and measurement configurations are used to develop methods for streamlining the analyses, such as considering which parameters may be kept common to multiple samples and how to deal with outliers resulting in substantially different optical properties and PV device performance. These patterns in parameter values may also predict success in accurately calculating PV device performance parameters from EQE simulations as well as develop strategies for analyzing large amounts of data sets.

EL-TuP-9 Determination of the Optical Constants and Thickness of Ultrathin Thermally Evaporated Iron Catalyst Films Using Spectroscopic Ellipsometry, ***Nicholas Allen****, M. Linford, R. Vanfleet, R. Davis,* Brigham Young University

Vertically aligned carbon nanotube (VACNT) forest growth is a catalytic chemical vapor deposition process that uses a thin-film iron catalyst on an alumina support. Iron catalyst thickness for VACNT growth is typically from ~1-10 nm and thickness strongly affects forest morphology. Transmission electron microscopy has been used to directly measure the thicknesses of thin iron/iron oxide films but is destructive and not easily used for routine process monitoring. Atomic force microscopy has also been used but requires the creation of an abrupt step edge in the film. Here we describe the use of spectroscopic ellipsometry for characterization of these very thin iron films. However, in this thickness range, the optical constants and thickness are not easily separated. The absorptive nature of the iron/iron oxide films adds further difficulty. In this study, a multi-sample ellipsometry analysis was performed using iron films of various thicknesses to obtain the optical constants of thermally evaporated iron. We also explored contrast enhancement by incorporating a silicon dioxide layer under the film being analyzed to enhance sensitivity to the optical constants.

EL-TuP-10 Elevated Temperature Model Dielectric Function of InAs Determined by Spectroscopic Ellipsometry, ***Preston Sorensen****, U. Kilic, R. Korlacki, M. Schubert,* University of Nebraska - Lincoln

We report a model dielectric function approach to determine and predict the elevated temperature (30-250°C) dielectric function of InAs across the spectral range of the near infrared to deep ultraviolet (0.73eV to 5.0eV). InAs is a III-V zincblende structure semiconductor with low-energy direct bandgap of 0.355eV and is of interest in long wavelength optoelectronic devices [1,3,4]. Determining accurately the thermal evolution of its optical properties, such as its complex index of refraction, bandgap energy, and band to band transitions permits for improved prediction of its thermal behavior in devices under operation. Also, knowledge of the dielectric function variation with temperature enables model-based analysis of spectroscopic ellipsometry data of InAs-based layer structures. Thermal perturbation of a crystal results in a small increase in the lattice constant of the material, altering the band structure, and therefore its dielectric function [4]. Spectroscopic ellipsometry permits measurement of the dielectric function of InAs. Measurements were taken from 30 ^{o}C to 250 ^{o}C at a single angle of incidence utilizing the temperature-controlled sample compartment of an atomic layer deposition system. The sample was also measured at room temperature at multiple angles of incidence in normal ambient to identify surface over layer effects. All ellipsometry data were modeled using a critical-point model dielectric function approach with implemented temperature dependencies of all the critical point model parameters [2,3]. We find linear evolutions of all critical-point model parameters versus temperature for the investigated temperature range. The obtained model parameters permit accurate prediction of the dielectric function of InAs at any temperature in the investigated range. Our result can be useful for model-based quantitative analysis of in-situ ellipsometry data obtained during atomic layer deposition growth of layer structures on InAs substrates.

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EL-TuP-11 Numerical Ellipsometry: Artificial Intelligence for Real-Time, *in Situ* Absorbing Film Process Control, ***Frank Urban****,* Florida International University*; D. Barton,* Florida International University Retired

Ellipsometry is a material analytical method in which the desired parameters, for example film thickness and index of refraction, are related to the instrument measurements through Maxwell's equations, light wavelength, and measurement geometry. Consequently, obtaining the desired parameters has required solving the model equations using a wide variety of methods. A commonly used method is least squares curve fitting, frequently the Levenberg-Marquardt method. This numerical method depends upon not only the model but also the initial estimates of solution, the possible interference of local minima, and the algorithm stopping conditions. Being iterative, it also can take significant time. The work here demonstrates the use of Artificial Intelligence in the form of a multilayer perceptron artificial neural network to avoid these problems and find solutions in the microsecond time scale. This non-iterative, stable, and fast performance lends itself to real-time, *in situ* monitoring of thin film growth. Examples for thin (up to 30 nm) films will be given using a multilayer perceptron configuration consisting of 4 input and 4 output neurons with two hidden layers of up to 20 neurons each. Solutions are performed at each wavelength independently and do not rely on fitting functions for optical properties.

EL-TuP-12 Massive Data Collection With A Pupil Plane Imaging Polarized White Light Interferometer, ***Alexander Boosalis,*** *Y. Wang,* Onto Innovation; *P. Vagos,* Onto Innovation, France; *Y. Liu,* Onto Innovation, Singapore; *G. Antonelli, N. Smith,* Onto Innovation

We present novel instrumentation capable of measuring the Jones matrix response of a sample across a large range of incident angles (0-55 degrees), sample rotation angles (0-360 degrees), and wavelengths (400-1000 nm) in less than 10 seconds. The result is a massive data set with over 600,000 individual data points. Development of this tool was spurred by the requirements of commercial chip manufacturing to collect and process a large amount data for optical critical dimension (OCD) metrology in the smallest possible time and within a shrinking measurement area. However, this instrument is increasingly applicable to the research community where development of metasurfaces, biaxial thin films, and other complex nanostructures requires measurement over a range azimuth angles to properly characterize. The instrument also has a small measurement spot size – less than 10 um in diameter – which is useful for both OCD metrology and prototype research nanostructures which tend to be hard to produce over large areas. We will demonstrate a prototype tool measuring an industry standard calibration scatterometry target with a 10um box size.

The white light interferometer is in a Linnik configuration with high numerical aperture objectives. By imaging the back focal plane of the sample objective to a camera we can collect a white light interferogram at every pixel that contains both reflection amplitude and phase information over a wide array of incidence angles. In this configuration the instrument lies somewhere between the capabilities of a polarized reflectometer and a rotating analyzer ellipsometer at each individual angle of measurement, with sensitivity to the entire Jones matrix but not the ability to measure the Jones elements specifically. We will show that rotating the system polarizer allows determination of the individual Jones matrix elements.

EL-TuP-13 Fast Spectroscopic Mueller Matrix Ellipsometry in the THz Range, ***Alexander Ruder,*** University of Nebraska - Lincoln; *S. Richter,* Lund University, Sweden; *P. Kuhne,* Linkoping University, Sweden; *V. Rindert,* Lund University, Sweden; *V. Stanishev,* Linkoping University, Sweden; *R. Korlacki, J. Olander,* University of Nebraska - Lincoln; *V. Darakchieva,* Lund University, Sweden; *M. Schubert,* University of Nebraska - Lincoln

We demonstrate a spectroscopic Mueller matrix ellipsometer in the THz wavelength range using rotating anisotropic optical components for polarization state generation and analysis. A solid state source and detector allow for time division multiplexing of individual wavelengths at kHz rates. Synchronous modulation of the source wavelength, polarization state generator, and polarization state analyzer allows for rapid acquisition of 4x4 Mueller matrix spectra. Calibration procedures and initial results for isotropic and anisotropic samples are discussed.

Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM

Multi-Modal & Multi-Dimensional Analysis

Moderators: Gustavo Trindade, National Physical Laboratory, UK, **Paul Mack**, Thermo Fisher Scientific, UK, **Tim Nunney**, Thermo Fisher Scientific, UK

8:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-1 Growth and Characterization of Large-Area 2D Materials***, **Glenn Jernigan**,* US Naval Research Laboratory **INVITED**

Nothing could be more coupled than Growth and Characterization. When two dimensional (2D) materials appeared on the radar of the scientific community (with the amazing properties of graphene), it was immediately obvious that large area samples would be needed. Exfoliating flakes was insufficient for the demands of scientific studies, in addition to not being viable should a commercial application be developed. Thus, the search began for growth methods to produce large-area 2D materials for large scale testing and development.

The Naval Research Laboratory has, over the past 15 years, pursued research programs in producing large areas of graphene, transition metal dichalcogenides (TMDs), boron nitride (BN), and other 2D materials. In every one of those programs, they began with surface analysis of composition, chemistry, and morphology of the grown films. The uniquely sensitive nature of x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and scanning tunneling and atomic force microscopy (STM and AFM) to 2D materials was necessary to measure the electrical, chemical, and physical properties obtained in the large area films and to understand what was observed in the exfoliated flakes. The production of large areas allowed "mass-scale" optical and electrical characterization, which then became a feedback loop in the search for new and interesting properties and relevant applications. In this presentation, I will show how we developed large-area graphene, by both epitaxial growth and chemical vapor deposition methods, TMDs, and other 2D materials for characterization and device utilization.

8:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-3 Using a Correlative Approach with XPS & SEM to Measure Functionalized Fabrics for Antimicrobial Applications***, **Tim Nunney**, H. Tseng,* Thermo Fisher Scientific, UK*; D. Marković, M. Radetić,* University of Belgrade, Serbia

Medical textiles are an indispensable component for a wide range of hygienic and healthcare products, such as disposable surgical gowns and masks, or personal protection equipment, with opportunities to provide further protection by engineering textiles with suitable medical finishing. While antibiotics are considered a viable option for their efficiency in treating bacterial infections, their abuse can result in adverse effects, e.g., bacteria resistance. Nanocomposites have emerged as a promising alternative to antibiotics, as the large surface-to-volume ratio and high activity helps attain the targeted antimicrobial efficiency by using tiny amounts of nanocomposites, and their biocompatibility and scalability are particularly advantageous for medical applications [1]. Thus, developing processing methods to integrate nanocomposites in the fabrics is essential for exploiting their properties for medical textiles.

In this study, polypropylene fabrics, alginate and copper oxides, were selected to develop novel antimicrobial nanocomposites based on various surface treatments, i.e. corona discharge and alginate impregnation, which led to improved fabrics hydrophilicity with functional groups introduced as binding sites for Cu(II), a precursor that formed Cu nanoparticles when reacted with reducing agents, i.e. NaBH4 and ascorbic acid. The composition of the fabrics after being treated with corona discharge and impregnation observed by XPS indicates the materials formed mainly consisted of C and O, attributed to the presence of a thin, hydrophilic layer and alginate, respectively, consistent with depth profiling measurements. Following Cu reduction, XPS mapping of the fabrics finds that, reacting with ascorbic acid resulted in formation of nanocomposites containing a mixture of Cu and Cu (II) oxides across the surface, which could be visualised by using SEM in the same locations. Excellent anti-microbial activity against Gram-negative bacteria E. coli, Grampositive bacteria S. aureus and yeast C. albicans was observed for the treated fabrics[2]. This result not only demonstrates a cleaner, and healthier approach for developing novel nanocomposites, but more importantly highlights the role of surface techniques in uncovering challenges in designing and engineering functional textiles.

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[2] D. Marković, H.-H. Tseng, T. Nunney, M. Radoičić, T. Ilic-Tomic, M. Radetić, Appl. Surf. Sci., 527, 146829, (2020)

9:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-4 Multi-Modal Analysis in Photoelectron Spectroscopy: From High-Resolution Imaging to Operando Experiments***, **Olivier Renault**,* CEA-Leti, France*; A. Benayad,* CEA, France*; N. Gauthier,* CEA-Leti, France*; R. Charvier,* ST Microelectronics, France*; E. Martinez,* CEA-Leti, France

Over the past years, the field of surface and interface analysis has been greatly expanded by new developments made possible by lab-scale instruments enabling higher excitation energies. These new developments are directly serving technological advances especially in the area of technologies in renewable energies and nanoelectronics, which are adressing more and more complex system requiring to go beyond traditional ways of characterizing surfaces and interfaces. Different dimensions are to be explored in multi-modal surface analysis : the depth dimension, the lateral dimension, and the dynamic dimension.

After a short review of some of the achievements towards enhancing the depth dimension by lab-scale hard X-ray photoelectron spectroscopy (HAXPES) and the lateral dimension using X-ray PEEM, we will present different application cases of *operando* HAXPES. Here, the material is analyzed as being part of a device operated *in situ* during the experiment, in conditions that are as close as possible to the final applications and where the interfaces can be studied in dynamic conditions. We will first review some results of *operando* HAXPES on resistive memories obtained with synchrotron radiation [1, 2] before presenting various lab-scale experiments [3, 4] and the current limitations to such approaches.

[1]B. Meunier, E. Martinez, O. Renault et al. *J. Appl. Phys*. **126**, 225302 (2019).

[2]B. Meunier, E. Martinez, O. Renault et al., *ACS Appl. Electron. Mater*. **3** (12), 5555–5562 (2021).

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9:20am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-5 Multi-Modal Analyses of Ultrasonic-Spray-Deposited Ultrathin Organic Bathocuproine Films***, J. Chen, **Juliet Risner-Jamtgaard**, T. Colburn, A. Vailionis, A. Barnum, M. Golding,* Stanford University*; K. Artyushkova,* Physical Electronics*; R. Dauskardt,* Stanford University

Bathocuproine (BCP) is a small organic molecule that is typically used as an ultrathin hole blocking interlayer (< 10 nm thickness) in organic solar cells and perovskite solar cells. The film is typically deposited via low-throughput vacuum thermal evaporation with an *in-situ* Quartz Crystal Monitor to measure film thickness. Open-air ultrasonic spray deposition for low-cost and large-scale deposition is an attractive alternative method for solution processing of BCP films, but the process lacks a comparable *in-situ* metrology. Given that the BCP film is transparent to visible light and ultrathin, it is important to utilize a multi-modal approach to evaluate optoelectronic and physical properties of the sprayed film.

A suite of characterization techniques that span a range of equipment complexity, measurement time, and measurement sensitivity are used to analyze the BCP films. We begin by demonstrating the limitations of the singular ellipsometry model[1] for BCP found in literature and motivate a need to rely on other techniques. Multi-modal analyses including X-Ray Reflectivity, Angle-Resolved X-ray Photon Spectroscopy (AR-XPS), Auger Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy with EELS are then performed on the sprayed BCP film. The advantages and disadvantages of each characterization technique are compared and discussed. We conclude that AR-XPS provides the most distinctive determination of individual layer thicknesses for a sample architecture consisting of silicon substrate/native SiO_x/BCP across the applicable range of AR-XPS from ~ 1-10 nm.

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9:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-6 Combinatorial Synthesis and High-Throughput Characterization of Pt-Au Thin Films Fabricated by Confocal Magnetron Sputter Deposition***, **David Adams**, R. Kothari, M. Kalaswad, C. Sobczak, J. Custer, S. Addamane, M. Jain, E. Fowler, F. DelRio, M. Rodriguez, R. Dingreville, B. Boyce,* Sandia National Laboratories

A few binary metal alloys are predicted to form thermally stable, compositionally segregated structures owing to the thermodynamic preference for minority species to collect and remain at grain boundaries established within the solid.(J.R. Trelewicz et al., PRB, 2009) When produced as a nanocrystalline thin film, these stable structures afford the potential to maintain excellent mechanical properties (e.g., high hardness) even after annealing to elevated temperature. Indeed, several systems, including $Pt_{.9}Au_{.1}$ thin films, are reported to develop thermally-stabilized, hard, nanocrystalline structures attributed to solute segregation at grain boundaries.(P. Lu et al., Materialia, 2019)

Future studies that seek optimal stoichiometry and/or preferred synthesis processes require access to a wide range of composition as well as an ability to vary key deposition parameters. Toward this end, our team reports on the challenges and the benefits of combinatorial synthesis for expediting the discovery of improved binary metal thin films. Our study utilized confocal sputter deposition wherein Pt and Au targets were individually sputtered via pulsed DC magnetron methods. Substrates (150 mm diameter wafers) were fixed in order to gain access to a wide compositional range for each deposition. The sputter power and cathode tilt orientation were then varied in subsequent depositions to access the nearly full binary metal compositional range. The binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films 2012), which simulates the transport of sputtered atoms within the process gas, helped guide the selection of these process parameters in order to achieve compositional goals in relatively few depositions. Notably, the binary compositions predicted by SiMTra closely matched (within a few molar %) the measured compositions determined by Wavelength Dispersive Spectroscopy completed in 112 different areas across each wafer. The various combinatorial Pt-Au films were further characterized by high-throughput Atomic Force Microscopy, automated X-ray Diffraction, fast X-ray Reflectivity, mapping four-point probe sheet resistance, and automated nanoindentation. These studies reveal how hardness, modulus, film density, crystal texture, and resistivity of combinatorial films varied with composition as well the atomistics of film deposition. Attempts to correlate key film characteristics with the kinetic energies and incident angles of arriving metal species (estimated by SiMTra) are discussed with a goal of improving fabrication processes.

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11:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-10 Optical and X-Ray Characterization and Metrology of Si/Si(1-X)Ge(X) Nanoscale Superlattice Film Stacks and Structures***, **Alain Diebold**,* SUNY Polytechnic Institute **INVITED**

As traditional scaling of transistors comes to end, transistor channels and capacitors are being stacked to form new 3D transistor and memory devices.Many of these devices are fabricated using films stacks consisting of multiple Si/Si(1-x)Gex layers known as superlattices which must be fabricated with near atomic precision.In this talk, we discuss how Optical and X-Ray methods are used to measure the feature shape and dimensions of these structures.The use of X-Ray methods such as ω-2θscans and reciprocal space maps provide layer thickness and stress characterization. We will use simulations to show how a buried layer with a different thickness or Ge concentration alters the data. Recent electron microscopy studies have quantified the stress at the interfaces of these superlattices.We will also discuss how Mueller Matrix spectroscopic ellipsometry (MMSE) based scatterometry is used to measure feature shape and dimension for the nanowire/nanosheet structures used to fabricate nanosheet transistors and eventually 3D DRAM.The starting point for optical scatterometry is determining the optical properties of stressed pseudomorphic Si(1-x)Gex.MMSE can be extended into the infra-red and into the EUV.In addition, small angle X-Ray scattering has been adapted into a method knows as CDSAXS which can be used to characterize these structures.This talk will be an overview of these methods.

11:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-12 Non-Destructive Depth Differentiated Analysis of Surfaces Using Ion Scattering Spectroscopy (ISS), XPS and HAXPES***, **Paul Mack**,* Thermo Fisher Scientific, UK

Recently there has been renewed interest in probing deeper into surfaces using HAXPES in addition to the more surface sensitive (soft X-ray) XPS. On modern XPS systems, with high sensitivity, the total sampling depth may be somewhere between 10nm and 15nm but HAXPES enables the analyst to look deeper, without having to destructively sputter the surface with ions. For a complementary, more comprehensive analysis, XPS and HAXPES can be combined with Ion Scattering Spectroscopy (ISS). ISS is far more surface sensitive than XPS, typically being thought of as a technique to analyse the top monolayer of a sample for elemental information.

In this work, the combination of XPS, HAXPES and ISS on a single tool has been used to give a non-destructive depth differentiated analysis of a range of samples, including a perovskite and an industrially relevant material containing multiple transition metals. The combination of all three techniques provides insight into the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface.

12:00pm **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-13 Towards Measurement of Molecular Shapes Using OrbiSIMS***, **Gustavo F. Trindade**, J. Vorng, A. Eyres, I. Gilmore,* National Physical Laboratory, UK

An OrbiSIMS [1] instrument features a dual analyser configuration with a time-of-flight (ToF) mass spectrometer (MS) and an Orbitrap™ MS, which confer advantages of speed and high-performance mass spectrometry, respectively. The ability to combine the MS performance usually found in a state-of-the-art proteomics and metabolomics MS with 3D imaging at the microscale and from nanolayers of <10 nm of material has proved popular in a broad field of application from organic electronics to drug discovery. For secondary ions to be efficiently transferred to the Orbitrap analyser, the sample is biased by a target voltage V_T necessary to match the acceptance window of the Orbitrap. Furthermore, the ions kinetic energy from the SIMS collision process must be reduced. Therefore, in the OrbiSIMS, a transfer system with helium gas at a pressure P_{He} slows the ions and reduces their kinetic energy distribution through inelastic collisions with gas atoms. Usually, an Orbitrap is used with an ambient pressure ion source and so here an extra gas flow of nitrogen is introduced that leads to an increase of pressure P_{N2} to compensate.

We conducted a systematic assessment of V_T and P_{He} and P_{N2} on the transmitted secondary ion intensities [2] and revealed a complex behaviour, indicating the possibility for additional separation of ions based on their shape, stability, and kinetics of formation. We showed that the V_T for maximum transmission of secondary ions will not be the same for all molecules of the same material and that sometimes multiple maxima exist. Here, we present recent progress towards the understanding of these phenomena and how we are leveraging it to measure molecular shape by using reference trisaccharides raffinose, maltrosiose and melozitose [3].

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[2] L. Matjacic *et al.*, “OrbiSIMS metrology part I: Optimisation of the target potential and collision cell pressure,” *Surf. Interface Anal.*, no. November 2021, pp. 1–10, 2021, doi: 10.1002/sia.7058.

[3] G.F. Trindade *et al.*, In preparation.

Applied Surface Science Division
Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-WeA

Quantitative Surface Analysis I

Moderators: David Cant, National Physical Laboratory, UK, **Peter Cumpson**, University of New South Wales, **Christopher Moffitt**, Kratos Analytical Inc, **Lev Gelb**, University of Texas at Dallas

2:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-1 Status of Efforts to Upgrade the Quality of Surface Analysis Data in the Literature***, **Donald Baer**,* Pacific Northwest National Laboratory

Multiple efforts are being undertaken to address a growing presence of faultysurface analysis data and/or analyses appearing in the literature. Issues include bad data, incorrect analysis, and highly incomplete reporting of instrument and analysis parameters. This talk describes the status of four efforts to address some of the issues. Recognition of this problem within the surface analysis community has increased with an understanding that both inexperienced users and increased use of surface analysis methods outside the surface analysis community contribute to the problem. The current efforts build upon decades of development and efforts by standards committees, excellent books and journal publications, websites, short courses, and other efforts. A collection of guides, protocols and tutorials addressing reproducibility issues with a significant *focus on XPS* was published in JVSTA in 2020/21. A second collection, *Reproducibility Challenges and Solutions II,* with a more general focus on Surface and Interface Analysis was initiated in 2022 and is being finalized. The second collection addresses several techniques, including SIMS, SPM, and UPS, and includes topics such as theoretical modeling and machine learning in data analysis. A second effort focuses on a part of the community less interested in general understanding but needs to answer specific surface analysis questions. A new type of paper called Notes and Insights is being published in the journal Surface and Interface Analysis with the objective to provide incremental bits of useful information of importance to non-expert analysts. Two additional activities are underway to assist with reporting issues. Examination of papers in multiple journals found that instrument and analysis related information needed to assess or reproduce data is often incomplete or absent. To assist authors in reporting instrument parameters, papers describing in some detail related families of commercial instruments are being prepared for Surface Science Spectra. These papers describe the instrument, major components, geometry and provide example data related to common data collection modes. Authors will be able to reference these papers and identify specific modes of instrument operation used in their research. Another parameter reporting activity concerns sample handling before analysis. ISO Technical Committee 201 is developing a series of documents (ISO 20579 parts 1 to 4) on what needs to be reporting regarding sample handling, storage, processing, and mounting for analysis. These standards describe what needs to be reported and contain informative annexes that provide information regarding the needs and challenges to proper sample handling to produce reliable useful surface analysis data.

2:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-2 The behavior of the Shirley background of the Ti 2*p* spectra across the Ti 1*s* edge***, **Dulce Maria Guzman Bucio**,* CINVESTAV-Unidad Queretaro, Mexico*; D. Cabrera German,* Universidad de Sonora, Mexico*; O. Cortazar Martinez, J. Raboño Borbolla,* CINVESTAV-Unidad Queretaro, Mexico*; M. Vazquez Lepe,* Universidad de Guadalajara, Mexico*; C. Weiland, J. Woicik,* National Institute of Standards and Technology*; A. Herrera Gomez,* CINVESTAV-Unidad Queretaro, Mexico

A wide variety of photoemission spectra display a step-shaped background, called the Shirley-type background, which should be accounted for in the total background signal for reliably assessing chemical composition. However, it cannot be modeled with any method based on extrinsic processes like the inelastic dispersion of the photoelectrons (e.g., Tougaard-type backgrounds). Although its physical origin is still unknown, experimental data suggest that the Shirley-type background is due to phenomena occurring inside the atom [1,2]. To gain insights into those phenomena, we studied the behavior of the Shirley-type background for the Ti 2*p* photoemission spectra.

In this work, Ti 2*p* photoemission spectra were acquired with Synchrotron light (at Beamline 7-2 at the Brookhaven National Laboratory) from a clean metallic titanium film (sputtered on a Si (100) substrate) capped with an ultra-thin aluminum layer. The spectra were collected with 44 excitation energies around the Ti 1*s* edge. By simultaneously fitting Ti 2*p* photoemission spectra obtained with excitation energies higher than the Ti 1*s* edge, we robustly determined the peak structure of the Ti 2p spectra. Outstandingly, the parameter of the Shirley-type background associated with the Ti 2*p* peak structure is modulated as the photon energy crosses the Ti 1*s* edge. The relation of this phenomenon with the physical origin of the Shirley background will be discussed. The $KVL_{2,3}$ Auger peaks—which overlap with the Ti 2*p* peaks—do not have a step-shaped background for most of the excitation energies.

Acknowledgments:

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3:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-3 Chemical Analysis of Multilayer System by Photoemission: The Binding Energy Reference Challenge***, **Thierry Conard**, A. Vanleenhove,* IMEC Belgium*; D. Desta, H. Boyen,* University of Hasselt, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces. It is most commonly performed using Al Kα radiation (1486.6 eV), which limits the analysis to the top 5-10nm. The recently developed laboratory-based hard X-ray photoelectron spectroscopes (HAXPES) provide new analysis options. They enable the analysis of thicker film structures and interfaces buried down to 20-50 nm depending on the photon energy and facilitate the analysis of fragile buried layers without ion-induced chemical damage.

Increasing the number of analyzed (insulating) layers enhances the risk of significant vertical differential charging and makes the repeatability of binding energy determination more challenging. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from HAXPES analysis. Vertical charge build-up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in 'simple' non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

In this work, we will examine the influence of measurement conditions in single and multiple layers systems relevant to the microelectronic industry on the determination of precise binding energies.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises oxide layers Si samples and metal/high-k/Si stacks including high-k materials as HfO_2 and Al_2O_3. The surface potential will be precisely set and monitored in situ by depositing a metallic layer (such as Ag) on top of the stack and applying an external potential instead of using an electron neutralization source. All experiments are performed in a PHI *Quantes* system and/or a Scienta Omicron *HAXPES Lab*, both equipped with two monochromatic X-ray sources: an Al Kα (1486.6 eV) and a Cr Kα (5414.8 eV - *Quantes*) or Ga Kα (9252.1 eV – *HAXPES lab*) X-ray source.

3:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-4 Where Are We on the Road-Map to Artificially Intelligent Interpretation of X-ray Photoelectron Spectra?**, *C. Moffitt,* Kratos Analytical Inc*; A. Roberts, J. Counsell, C. Blomfield,* ***Kevin Good****, K. Macak,* Kratos Analytical Limited, UK

Robust peak identification is crucial for accurate sample analysis using X-ray photoemission spectroscopy (XPS). Automation of peak ID enhances this process by minimizing user error and bias. Current acquisition software offers improved computer-derived peak identification from unknown samples, instilling confidence in the correct identification of elements. Moreover, this forms the foundation for an automated sample analysis workflow known as Data-dependent Analysis (DDA). DDA involves identifying peaks in a survey spectrum and subsequently acquiring high-resolution spectra from major components. A recent User survey revealed that a significant majority of users rely on the large area survey acquisition mode as a starting point for analysis.

To provide a metric for confidence in the DDA process, existing spectral analysis data, which includes the element composition information, is used to generate reference spectra for testing purposes. These reference spectra serve as the basis dataset against which the performance of the automated analysis algorithm can be evaluated. By comparing the results of the algorithm with the reference spectra, statistical parameters can be calculated to assess the algorithm's precision, sensitivity, specificity, and accuracy in identifying elements of unknown spectra.

For experienced analysts, DDA serves as a time-saving acquisition method, while for inexperienced analysts, it provides assurance in accurate peak identification and appropriate high-resolution spectra acquisition. Here we highlight current status of automated XPS data acquisition in relationship to the 'expert system', championed in the early 2000's and full AI interpretation of XPS spectra of the future.

4:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-7 Thin Film Analysis by XPS: Quantitative Analyses Using Physics-Based and Machine-Learning Approaches***,* ***Lev Gelb****, N. Castanheira, A. Walker,* University of Texas at Dallas

We present progress towards quantitative analysis of XPS data using both model-based "fitting" approaches and machine learning methods. Two separate applications are considered.

The first concerns the simultaneous extraction of both compositional profiles and sputtering parameters from XPS sputter depth-profiles of multilayer films. Depth-profile data are routinely processed to provide "fractional composition vs ion dose" profiles, but such analyses typically assume the sample is homogeneous in the probed region, which is not true near interfaces, and cannot precisely convert between units of ion dose and depth without extensive calibration data. Our approach is to first construct analytical models for both the sample structure and for the sputtering process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) that are most likely given the observed apparent fractional composition profiles. This is done numerically, by iteratively comparing simulated and observed apparent composition profiles. The only additional required inputs are the inelastic mean free paths for each tracked peak in each material present. The efficacy of this approach is demonstrated using both synthetic and experimental data sets, and various model improvements (sputter-induced mixing, *in situ* chemical reactions) are discussed.

The second application concerns the application of machine-learning tools to remove the inelastic scattering background from XPS spectra in order that accurate peak areas can be obtained. Our approach here is to generate a training data set which consists of a thousands of simulated XPS spectra with and without inelastic scattering included. This is accomplished using the SESSA software package[1]. This data set is then used to train a neural network algorithm to output a "no-background" spectrum from an input "with-background" spectrum; this output spectrum can then be used to compute peak areas for compositional analysis. The training set generation methodology and network structure are discussed, and application of the tool to both simulated and experimental spectra is demonstrated.

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4:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-8 Room Temperature Ionic Liquids as Reference Materials for Photoelectron Spectrometers***,* ***Benjamen Reed,*** National Physical Laboratory, U.K.*; J. Radnik,* BAM Berlin, Germany, UK*; A. Shard,* National Physical Laboratory, U.K.

Room-temperature ionic liquids (RTILs) are materials consisting of organic salts that are liquid below temperatures of 100°C and are used in several fields including electrochemistry,[1] pharmaceutics, and medicine.[2] RTILs have several notable properties that make them ideal for X-ray photoelectron spectroscopy (XPS) analysis. They have an extremely low vapor pressure and high surface tension, and so can be analysed using conventional XPS under ultrahigh vacuum without the need for near-ambient pressure instrumentation. Also, when deposited in a recessed sample holder, the meniscus of an RTIL will be perfectly flat meaning that there are no contributions from sample topographic effects. Finally, and most importantly, they are highly homogeneous and have well-defined stoichiometries.[3]

These properties make RTILs potential reference materials for validating the intensity calibration of a photoelectron spectrometer. RTILs with non-coordinating bistriflimide (NTf_2) anions (e.g. $PMIM^+NTf_2^-$) or dimethyl phosphate (DMP) anions (e.g. $MMIM^+DMP^-$) are such candidates, with core levels up to ~800 eV binding energy, making them apt for verifying the quantification of light elements, especially for organic materials.[4,5]

To accurately determine peak areas, however, requires the principal and secondary photoelectron signals to be deconvolved. Previous attempts by multiple laboratories using different quantification methods give a mean atomic composition within 1 at.% of the known stoichiometry, but some individual elements (such as fluorine) exhibit differences greater than 1 at.% because the elastic and inelastic secondaries are not suitably deconvolved. Attention must be paid to the energy loss function that defines the inelastic background over the full energy range of an XPS spectrum so that a suitable Tougaard background subtraction can be applied.[6] Here we present a study on several RTILs and discuss how they may be used to validate an XPS intensity calibration and provide confidence in measurements to XPS instrument operators.

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[3]E. F. Smith, I. J. Villar Garcia, D. Briggs et al., *Chem. Commun*. **45**, 5633 (2005).

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[5]X. Knigge and J. Radnik, *Surf. Sci. Spectra***30**, 014006 (2023).

[6]M. P. Seah, I. S. Gilmore, and S. J. Spencer, *Surf. Sci.* **461**, 1 (2000).

5:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-9 Fractional Coverage Analysis of Monolayers with XPS and Non-Destructive Depth-Profiling with Combined Soft and Hard X-Rays***,* ***Norbert Biderman****, K. Artyushkova, D. Watson,* Physical Electronics USA

X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. Angle-resolved XPS (AR-XPS) has been used to determine composition of depth profiles and layer thicknesses, traditionally with Al Kα (1486.6 eV) X-ray beams for depths up to 5-10 nm below the surface. In recent years, new AR-XPS capabilities have been added to Physical Electronics XPS scanning microprobe instruments including Cr Kα (5414.8 eV) hard X-ray photoelectron spectroscopy (HAXPES) that can probe buried interfaces up to 15-30 nm below the surface. Coinciding with the HAXPES development, the StrataPHI analysis software was developed to reconstruct quantitative, non-destructive XPS/HAXPES depth profiles from angle-dependent and single-angle photoelectron spectra.

In this talk, we will show that the StrataPHI software has been further developed to combine Al Kα and Cr Kα XPS and HAXPES data within a single depth profile to enhance extracted analytical information from various depths below the surface. We will explore the method of the combined technique as well as its application to multilayered thin film samples. The updated StrataPHI software also includes a fractional coverage analysis mode, relevant in situations where ultra-thin films exist as discrete islands – commonly observed in early thin-film deposition stages on the substrate rather than as a continuous, uniform film. A model system of discrete molybdenum sulfide (MoS2) monolayer triangles deposited on SiO2/Si substrate will be discussed.

Such added StrataPHI capabilities allow for scientists and engineers in metrology and research & development to analyze multi-layered thin films and ultra-thin films rapidly and non-destructively without potentially damaging ion beam sputtering that might otherwise be required to depth-profile or sputter-clean adventitious contamination off the surface.

5:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-10 Reassessing the Reduction of Ceria in X-Ray Photoelectron Spectroscopy***, **David Morgan**,* Cardiff University, UK

Given its excellent redox abilities, the use of cerium dioxide (CeO_2, ceria) and related materials in catalysis is widespread [1]. This Ce^{3+}/Ce^{4+} redox shuffle allows for great catalytic ability and a method of correlation of catalytic activity to the state of ceria [2–4].Given that catalysis is a surface mediated process, XPS is critical in the analysis of pre- and post-mortem materials.

Over the years there has been debate on the degree of reduction of CeO_2 during XPS analysis. Therefore, in continuation of our work on understanding the reduction of materials in modern spectrometers [5], we have investigated different cerium oxide preparations and shown that not only is the rate of reduction dependent on instrument type and experimental configuration (and hence appropriate analysis protocols should be implemented), but is also related to the morphology of the cerium which may, at least in part, account for the discrepancies in the degree of reduction in the literature. It is postulated that reduction rates could be used to indicate likely ceria morphology where other analysis is unavailable.

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Acknowledgements

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5:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-11 Using High Sensitivity – Low Energy Ion Scattering Spectroscopy (LEIS) to Unravel the Complex Nature of High Entropy Alloys***, **Matthias Kogler**, C. Pichler,* Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria*; M. Valtiner,* Vienna University of Technology, Austria

Complex metallic materials such as Multi-Principal Alloys (MPEAs) and High Entropy Alloys (HEAs) have emerged as a promising class of materials given their unique inherent characteristics. Excellent mechanical, thermal, and corrosion properties allow for a broad spectrum of applications. However, due to the multi-element nature of these alloys, characterisation of the composition and microstructure proves to be a challenging task.

Especially with regard to corrosion-protective passivation films, the complex correlations with the corrosion behaviour are fully unclear to date, and require an in-depth atomic level characterisation and rationalisation. However, the precise layer by layer structure of such passive films is particularly demanding to assess, since traditional techniques such as XPS (X-ray photoelectron spectroscopy) or AES (Auger electron spectroscopy) have analysis penetration depths of several nanometres and cannot reach atomic layer resolution. However, to fully understand and quantify the passivation layer structure, such an atomic layer resolution of the surface region is necessary, due to the complexity of HEAs.

In order to obtain an exact understanding of the atomistic mechanism at the monoatomic layer level, High-Sensitivity - Low Energy Ion Scattering Spectroscopy (HS-LEIS), was applied, which provides the required monolayer sensitive resolution to study the passivation layers of such complex multi-component alloys. The unique surface sensitivity combined with the implementation of in-situ treatment methods enabled the real-time study of oxide layer growth, as well as the analysis of temperature-dependent changes in the elemental surface composition. Due to the high resolution achieved by static and dynamic sputter depth profile modes, we could determine the exact composition of the HEA passivation layer with resolution on atomic monolayer scale.

The findings provide the potential to significantly advance the current understanding of the passivation behaviour of MPEAs and HEAs, and the development of novel metallic materials with superior properties. Valuable insights for understanding the material characteristics for those highly advanced materials could thereby be generated.

Applied Surface Science Division
Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-ThM

Quantitative Surface Analysis II

Moderators: Samantha Rosenberg, Lockheed Martin, **Thierry Conard**, IMEC, Belgium, **Benjamen Reed**, National Physical Laboratory, UK

8:00am **AS+CA+EL+EM+SE+SS+TF-ThM-1 OrbiSIMS: Signal, Noise and Transmission Are Three Sides of a Metrology Triangle**, *G. Trindade, Y. Zhou, A. Eyres,* National Physical Laboratory, UK; *M. Keenan,* Independent; ***Ian Gilmore***, National Physical Laboratory, UK

In metrology, the science of measurement, a “metrology triangle” approach is used to provide a secure foundation. For example, the Quantum Metrology Triangle links Voltage, Resistance and Current through the Josephson Effect and the Quantum Hall Effect.

The OrbiSIMS[1], introduced in 2017, has become increasingly popular for biological and material sciences studies owing to its ability to give high confidence in molecular identification (mass resolving power > 240,000 and mass accuracy < 2 ppm) simultaneously with high confidence in localisation (micrometre scale spatially and nanoscale in depth). With a growing number of instruments internationally there is an increased need for metrology for reproducible measurements. We will show how Signal, Noise and Transmission form three sides of a metrology triangle that combine to enable better measurement. In a recent comprehensive study of the noise in an Orbitrap mass spectrometer, a probabilistic model was developed.[2] A region of the intensity scale is described by Poisson statistics allowing the scaling parameter, *A*, that relates ion current to the number of ions in the trap to be determined. A true signal intensity scale is then established which allows the useful yield of atoms in an implant layer to be measured. Through comparison with time-of-flight and magnetic sector instruments the fractional ion transmission is determined.[3] We will discuss how Signal and Transmission combine to understand matrix effects in biological sample preparation and how understanding Signal and Noise are important for data analytical methods.

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3. Y. Zhou, A. Franquet, V. Spampinato, G. F. Trindade, P. van der Heide, W. Vandervorst and I S Gilmore, in preparation.

8:20am **AS+CA+EL+EM+SE+SS+TF-ThM-2 Contribution of Imaging X-Ray Photoelectron Spectroscopy to Characterize Chrome Free Passivation Nano-Layer Deposited on Food-Packaging Tinplate: Composition and Chemical Environment**, *E. Ros,* ***Vincent Fernandez***, CNRS, France; *N. Fairley,* CASAXPS, UK; *B. Humbert, M. Caldes,* CNRS, France

To protect metal from corrosion, passivation layer are widely used in food-packaging industry. Those Nano-metric protections create a thin oxide Nano-layer on the metal surface, making it less oxidisable. Common passivation are composed by chromium oxide[1] , using hexavalent chromium as a reagent and reducing it. However, because of the toxicity of Cr(VI), European Union is gradually forbidding.Chromium Free Passivation Alternative is based on transitions metal oxides (Sn, Ti, Zr, Mn) and polymers. These samples present some roughness in few micron range observed by Atomic Force Microscopy.XPS Imaging were perform at different binding energy to allow extracting spectrum in each pixel over the eight (Mn 2p, O 1s, Sn 3d, Ti 2p,N 1s, C 1s, P 2s and Zr 3d) XPS core level process. This study show an anti-correlation between atomic concentration of Titanium and Tin Fig(1). We observe a ratio Sn oxide Sn metal homogeneous and independent of the Ti, Sn ratio More over using the vector method [2], [3] concurrently to height XPS core , we could extract two different chemical environments spectrum. The linear Least Square combination of theses 2 spectrum allow us to model 131072 regions. To extract information form XPS data on heterogynous sample the combination of XPS imaging energy scan measurement with the vector method is a promising way. These results bring the useful information about different thin layer deposition steps. Imagerie XPS results are in agreement with Raman imagerie analysis

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8:40am **AS+CA+EL+EM+SE+SS+TF-ThM-3 Cryo-Xps for Surface Characterisation of Nanomedicines**, ***David Cant***, National Physical Laboratory,, UK; *Y. Pei,* National Physical Laboratory, UK; *A. Shchukarev, M. Ramstedt,* University of Umea, Sweden; *S. Marques, M. Segundo,* University of Porto, Portugal; *J. Parot, A. Molska, S. Borgos,* SINTEF, Norway; *C. Minelli, A. Shard,* National Physical Laboratory, UK

Nanomedicines are an area of great interest for current and future pharmaceutical development. The use of nanoparticles to act as carriers for a therapeutic load has the potential to significantly improve medical outcomes, for example by allowing a therapeutic agent to circulate within the body for longer, or by allowing targeted delivery of a drug to a specific site. Such nanomedicines often rely on specific functional coatings to achieve their desired impact; for example the majority of nanomedicines currently available on the market utilise a poly-ethylene glycol (PEG) surface coating for its ‘stealth’ properties, helping nanomedicines evade the body’s clearance mechanisms. Accurate measurement of the surfaces of such nanomaterials is therefore of great importance, yet direct, quantitative surface chemistry measurements are not commonly available, and vacuum-based analysis methods such as XPS are unlikely to provide a representative measurement of the particles in their hydrated state.

Here we present to the best of our knowledge the first use of Cryo-XPS to provide direct, quantitative measurements of the surface chemistry of nanomedicines in a hydrated state. Two nanomedicine systems were measured: a drug-carrying polymer nanoparticle; and an mRNA loaded lipid nanoparticle. Both systems possessed a supposedly PEG-terminated surface, and were measured using XPS in both aqueous cryogenic state, and dry drop-cast onto a substrate. The results of these measurements clearly demonstrate that while the PEG surface cannot readily be observed in the dry state, the cryogenic measurements exhibit spectra that are consistent with the particle being measured in a hydrated condition.

9:00am **AS+CA+EL+EM+SE+SS+TF-ThM-4 Redox XPS as a Means to Address Some XPS Reproducibility Challenges**, ***Peter Cumpson***, University of New South Wales, Australia

The challenge of better understanding of increasingly-complex specimens in surface analysis has been highlighted recently[1,2,3,4]. Especially at a time of high throughput XPS instruments and broadening of the (non-specialist) user community. An AVS survey conducted in 2018 found that 65% of those responding identified reproducibility as a significant issue [5].

There is an analogy to be made with some radically–different technologies. Machine Learning makes more sense of a moving image than a single snapshot, even if the snapshot were to come from a larger, better calibrated camera. Yet somehow we expect greater calibration precision, reference data and rigorous procedures to be the only route to reliable understanding of single spectra.

Generating a sequence of spectra from a progressively chemically-modified surface can remove many ambiguities that can otherwise cause misinterpretation. Such sequences thereby help with rapid understanding of the unmodified surface. On the theme of “Two is Better than One: Breaking Barriers with Coupled Phenomena” we present results from coupled stepwise oxidation/reduction of the surface and XPS to resolve such ambiguities for a wide range of materials and problems. Gas-phase oxidation agents are used to move through the redox states of a specimen in a controllable way, taking advantage of the logarithmic growth of oxide thickness. What is more, this oxidation is easy to implement in the entry-locks of modern XPS instruments through the use of vacuum ultraviolet light (VUV) and the *in situ* generation of ozone and gas-phase hydroxide free radicals. In the past there have been many studies of how particular materials react to ozone exposure at their surfaces, often employing XPS. Here we reverse this, and use ozone (and VUV) exposure to simplify the

interpretation of spectra from a wide range of unknown materials, we think for the first time.

[1] D R Baer et al, J. Vac. Sci. Technol. A 39, 021601 (2021); https://doi.org/10.1116/6.0000873

[2] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061204 (2020); https://doi.org/10.1116/6.0000685

[3] G. H. Major et al, J. Vac. Sci. Technol. A 38, 061203 (2020) https://doi.org/10.1116/6.0000377

[4] D R Baer and M. H. Engelhard, Journal of Surface Analysis Vol. 26, No.2 (2019) pp. 94-95.

[5] D R Baer, J F Watts, A Herrera-Gomez, K J Gaskell, Surf Interface Anal. 2023; 1- 9. doi:10.1002/sia.7194

9:20am **AS+CA+EL+EM+SE+SS+TF-ThM-5 Sub-Nanometer Depth Profiling of Native Metal Oxide Layers Within Single Lab-XPS Spectra***, Martin Wortmann, N. Frese,* Bielefeld University, Germany*; K. Viertel,* Bielefeld University of Applied Sciences and Arts, Germany*; D. Graulich, M. Westphal, T. Kuschel,* Bielefeld University, Germany

Many metals form nanometer-thin self-passivating native oxide layers upon exposure to the atmosphere, which affect their interfacial properties and corrosion behavior. Such oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). Here we propose a simple and accessible depth profiling approach for oxide layers with sub-nanometer depth resolution from single lab-XPS spectra. Metals and their oxides can be distinguished by a binding energy shift to quantify their distinct signal contributions. Analogous to the widely used Hill equation we utilize the known photoelectron's inelastic mean free path to calculate the characteristic oxide layer thickness. However, in contrast to the Hill equation we analyze not only one, but all orbital energies in the XPS spectrum to develop a model that accounts for a depth-resolved concentration profile at the oxide-metal interface. The proposed model not only improves the accuracy and reproducibility of earlier methods but also paves the way for a more holistic understanding of the XPS spectrum.

9:40am **AS+CA+EL+EM+SE+SS+TF-ThM-6 A Tag-and-Count Methodology Based on Atomic Layer Deposition (ALD) and Low Energy Ion Scattering (LEIS) for Quantifying the Number of Silanols on Fused Silica***, Josh Pinder,* Brigham Young University

The concentration of surface silanols governs many of the properties of glass and fused silica surfaces including surface wetting, surface contamination rates, and thin film adhesion. Indeed, the concentration of surface silanols is impactful for diverse fields such as atomic layer deposition (ALD), chromatography, catalysis, and displays. Accordingly, various analytical and theoretical methods have been employed to determine the number of silanols on surfaces, including density functional theory, FTIR, thermogravimetric analysis, and temperature programed desorption mass spectrometry. However, many of these methods are better applied to particulate materials than surfaces. In this presentation, we discuss a method for directly

measuring the concentrations of surface silanols on silica-containing surfaces via a tag-and-count methodology. This approach is based on tagging surface silanols by ALD via a single pulse of dimethylzinc or diethylzinc and then quantifying the number of tags (zinc atoms) using high

sensitivity-low energy ion scattering (HS-LEIS). Our method yielded the literature value for both fully hydroxylated fused silica and also fused silica that had been heated to 500, 700, and 900 C. We see this capability as enabling for all who work with glass, fused silica, and silicon wafers,

including for ALD.

11:00am **AS+CA+EL+EM+SE+SS+TF-ThM-10 ASSD Peter M. A. Sherwood Mid-Career Professional Awardee Talk: Providing Fundamental Mechanistic Insights Into Single-Site Catalytic Reactions***, Jean-Sabin McEwen*[1]*,* Washington State University **INVITED**

The single atom limit achieves the ultimate degree of material efficiency for supported metal catalysts. To this end, the ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we provide new atomistic insights regarding the "44" Cu surface oxide through the integration of synchrotron-based X-ray Photoelectron Spectroscopy (XPS) measurements, Synchrotron X-ray Diffraction measurements (SXRD), Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) techniques. We also quantify the low-temperature CO oxidation kinetics on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure that arises when we further oxidize the "44" structure. Using STM, CO temperature programmed desorption (TPD), and DFT techniques, we determine that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings. Furthermore, we determine the state of the Pt single atoms before, during, and after reaction through a combination of theoretical and experimental techniques. We also correlate ambient pressure experiments, surface science measurements and first principles-based calculations to demonstrate that Pt/Cu(111) single-atom alloys (SAAs) oxidized with varying degrees of O_2 exposure can be reduced with H_2 with reasonable kinetics (hours). This is in contrast to oxidized pure Cu(111) where such reduction is very slow (days). We further contrast the catalytic properties of Rh/Cu(111) SAAs with varying degrees of O_2 exposure to the those of Pt/Cu(111) SAAs. Finally, we report the effects of a copper oxide thin film toward the segregation of noble metal single-atoms on Cu (111) using DFT.

11:40am **AS+CA+EL+EM+SE+SS+TF-ThM-12 Beyond the Physical Origin of the Shirley Background in Photoemission Spectra: Other Predictions of the Interchannel Coupling with Valence Band Losses Mechanism***, Alberto Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

The physical mechanism proposed in our 2017 paper about the origin of the Shirley background in photoemission spectra[1] es based on interchannel coupling[2] but with the important addition of energy losses in the valence band.[3] Besides the Shirley background, it is possible to derive other predictions of the interchannel Coupling with Valence Band Losses mechanism (ICLM). Two of them are discussed in this paper: 1) the quantitative relation between Auger peaks and the Shirley background and 2) the conduction-band-like structure of the extended region of the Shirley background.

[1] A. Herrera-Gomez et al. Surface and Interface Analysis 50(2), 246–252 (2018).

[2] E.W.B. Dias et al. Phys Rev B 78(2), 4553–4556 (1997).

[3] http://www.qro.cinvestav.mx/~aherrera/reportesInternos/unknownOriginShirley.pdf

12:00pm **AS+CA+EL+EM+SE+SS+TF-ThM-13 Aging of Hydrophilicity in a Nano-Textured SS316 Thin Film Fabricated by Magnetron Sputtering***, **Pakman Yiu**,* Ming Chi University of Technology, Taiwan*; J. Chu, J. You,* National Taiwan University of Science and Technology, Taiwan

According to the structural zone model by J.A. Thronton[1], we may manipulate the surface morphology of a thin film by altering the deposition temperature and vacuum. Therefore in this study, we prepared a series of SS316 thin film by magnetron sputtering under different Argon working pressure. Resultant thin film possessed a pressure dependent nano-textured surface which was dependent on working pressure. Furthermore, we discovered that the textured surface was highly hydrophilic (water

[1] **ASSD Peter Sherwood Award**

contact angle <15 degrees). The hydrophilicity could be attributed to the combinitorial contribution of surface roughness and capillary effect. However, we also discovered that the hydrophilicity aged with time, where after 21 days the surface turned hydrophobic with water contact angle >90 degrees. XPS studies on both as-deposited and 21-days stored sample films revealed that there was a Carbon-rich surface layer on the surface which grew with time. Interestingly when we tried to clean the surface with Argon atmospheric plasma, the hydrophilicity was almost fully restored. Results revealed that the aging of hydrophilicity may due to the fact that nano-surface texture gathers hydrocarbons in the atmosphere, which eventually formed an extra film that altered the surface wetting property. Understanding the aging mechanism and method of ecovery may contribute to the development of a long-lasting hydrophilic surface, which is very useful in applications such as self-cleaning surface and medical apparatus[2,3]

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[2] A. Syafiq, B. Vengadaesvaran, A.K. Pandey, Nasrudin Abd. Rahim, J. Nanomater. 2018 (2018) 6412601.

[3] M. Xiao, Y.M. Chen, M.N. Biao, X.D. Zhang, B.C. Yang, Mater. Biol. Appl. 70 (2017) 1057–1070.

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