

Applied Surface Science Division Room A211 - Session AS+BI+RA-MoM

Quantitative Surface Analysis I/Reproducibility Issues in Quantitative XPS

Moderators: Donald Baer, Pacific Northwest National Laboratory, Mark Engelhard, Pacific Northwest National Laboratory

8:20am **AS+BI+RA-MoM1 Improving Accuracy in Quantitation by XPS: Standards, Cross-sections, Satellite Structure, C. Richard Brundle, C.R.Brundle & Associates; P.S. Bagus, University of North Texas; B.V. Crist, XPS International LLC** **INVITED**

Determining elemental composition by XPS requires determining relative peak intensities from the elements concerned, and then normalizing using Relative Sensitivity Factors (RSF's). Such RSF's are usually generated from standard materials using the intensity from the "main" peak only and ignoring any associated satellite structure (shake-up, shake-off, and multiplet splitting components) intensity. In the seminal paper by Wagner, et al, (1) this resulted in a conclusion that the calculated Li(1s) photoionization cross-section, σ , (2) was too low by ~40%, relative to F(1s). This apparent discrepancy cast doubt on the claimed 5% accuracy of the calculated σ values for low Z elements (2). We show that this is incorrect. The discrepancy is due, primarily, to the fact that Li(1s) loses almost zero intensity from the main peak into associated satellites, whereas for F1s it is substantial, *spreading over 100eV to lower KE*. A calculated σ always refers to the *total* intensity of photoemission from the orbital concerned, including any intrinsic satellite structure. In addition, the experimental Li(1s) peak intensity in Wagner, et al. (1) was actually *overestimated*, owing to inclusion of overlapping satellite structure spreading from the nearby F(2s) peak. For the 1s intensities of the first row elements, a crude theoretical approximation predicts the total intensity lost from the "main" peak to satellites quite well. It involves an exponential dependence on the number of valence shell electrons present, which for Li+ of LiF, is zero, and for F- is 6 (the filled 2p shell), yielding values of zero loss for Li+ and 20-30% for F-. Full *ab initio* quantum calculations for these ions support the crude estimate (calculated Li+ losses are 1.4%; F- losses are 22.7%). In contrast to earlier claims to the contrary(3), satellite losses, for elements across the periodic table, vary widely from core-level to core level, element to element, *and most critically with the bonding situation of an element (see, for example ref 4)*. Thus any "universal" element RSF's, using main peak intensities only, though semi-quantitatively useful, are inherently limited in potential accuracy achievable, sometimes by up to a factor of 2. What is needed, for improved accuracy, are sets of RSF's appropriate to different bonding situations. Such sets would be particularly useful for the current large inexperienced XPS user base. We attempt to give guidelines.

C.D. Wagner, et al, Surf. Interface Anal. **3**, 211, 1981

J.H. Scofield, J. Elec. Spec. **8**, 129, 1976

V.G. Yarzhemsky, et al, J. Elec. Spec. **123**, 1, 2001

P. S. Bagus, E. Ilton, and C. J. Nelin, Catalysis Letters, **148**, 1785, 2018

9:00am **AS+BI+RA-MoM3 A Rigorous Approach to the Calculation of the Uncertainties in XPS Analysis, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, México; Orlando Cortazar-Martinez, CINVESTAV-Unidad Queretaro, Mexico**

One of the most important applications of X-ray photoelectron spectroscopy (XPS) is the characterization of the chemical composition of solids near the surface. However, the proper assessment of the associated uncertainties has remained an elusive problem. One of the issues is that the total uncertainty comes from various sources: the experimental data (peak intensities), parameters theoretically calculated (cross-section, mean-free-path), and parameters associated to the XPS equipment (angular and kinetic energy transmission functions).

The uncertainty on most of these parameters should be treated as systematic errors. The most important non-systematic uncertainty comes from the peak intensities [1]. It is a common practice in XPS data peak fitting to first subtract the background and then peak-fit the backgroundless data (*static* approach [2]). This approach prevents the use of the covariance matrix to calculate uncertainties because the covariance with the parameters defining the background cannot be accounted. It is only under the *active* approach [2] that it is possible to account for the covariance with the background parameters because the background is optimized in conjunction with the peak parameters. In this paper, the

assessment of the uncertainty on the peak intensities will be treated in detail, as well as the total uncertainty on the composition.

[1] A. Herrera-Gomez, A rigorous approach to the calculation of the uncertainties in XPS analysis (Internal Report), Internal Report, Internal Report. CINVESTAV-Unidad Queretaro, n.d. <http://www.gro.cinvestav.mx/~aherrera/reportesInternos/uncertaintiesXP S.pdf>.

[2] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. **46** (2014) 897–905. doi:10.1002/sia.5453.

9:20am **AS+BI+RA-MoM4 Gross Errors in XPS Peak Fitting, Matthew Linford, V. Jain, G.H. Major, Brigham Young University**

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. It is widely used in numerous areas of research and technology. Many research groups and individuals are skilled at analyzing XPS data. However, too much of what has appeared and continues to appear in the literature is of at best questionable value and accuracy. In this talk, I will discuss some of the all too common gross errors. Both correct and incorrect examples of each of the following will be shown. (i) Not plotting the data according to international convention of binding energy increasing to the left. (ii) Fitting and interpreting data that are far too noisy to be interpreted. (iii) Labeling noise as chemical components. (iv) Not showing the original data – only showing the synthetic (fit) peaks and their sum. (v) Not plotting the sum of the fit components with the original data. (vi) Having widely varying peak widths in a fit. (vii) Having the baseline completely miss the noise on either side of the peak. (viii) Not collecting data over a wide enough energy window to see a reasonable amount of baseline on both sides of the peak envelope. (ix) In a C 1s spectrum, reversing the labeling on the C-O and C=O peaks, and other mislabeling issues. The C 1s peak envelope is well understood so there shouldn't be huge mistakes here. (x) Not taking into account spin-orbit splitting when it is necessary. (xi) In a comparison of spectra, having widely differing peaks and peak positions for components that are supposed to be the same between the spectra.

9:40am **AS+BI+RA-MoM5 Improved Energy Referencing in XPS, Hagai Cohen, Weizmann Institute of Science, Israel**

Basically, energy referencing in XPS relies on an absolute reference provided at the back contact of the sample: the electrical ground. If poor connectivity is encountered between the studied surface and ground, reference signals may be used to derive correction terms for the energy scale, such as to get the proper binding energies for elements of interest. Unfortunately, in many cases this procedure fails to accurately address differential charging effects, namely local and temporal variations in the surface charge and the related electrostatic potential.

In the present work, a method for introducing a second absolute/external reference is described. The technical improvement is proven to be mandatory. It enables advanced analyses of binding energies, which refines the chemical analysis significantly. The method further reveals intriguing cases in which the x-ray induced charging does not follow the trivially expected behavior. On top of that, an access to rich electrical information is realized as soon as a second reference is introduced, thus expanding the XPS capabilities into new areas. Measurements of the inherent inner fields in semiconductors and the reliable derivation of device band diagrams, free of the beam-induced artifacts, are just a few examples to be mentioned.

10:00am **AS+BI+RA-MoM6 How to Avoid Errors in the Interpretation of XPS Data?, Andreas Thissen, P. Dietrich, SPECS Surface Nano Analysis GmbH, Germany; W.E.S. Unger, Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany), Germany**

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

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

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even more, data quality becomes transparent also in times of open source publications and open data repositories.

This paper summarizes the challenges of data handling, data treatment, data storage, parameter-data correlation, expert systems for data acquisition, reporting assistance and tracking and authorization tools for sensitive data. In summary future perspectives and suggestions are discussed for improved data repeatability and data reliability.

10:40am **AS+BI+RA-MoM8 Misinterpretations in the Spectroscopic Analysis of Heterogeneous Materials and Defected Structures**, *Lisa Swartz, K. Artyushkova, J.E. Mann, B.W. Schmidt, J.G. Newman*, Physical Electronics

Analysis of samples where lateral heterogeneities can be present at a variety of scales poses a challenging spectroscopic task. In routine applications of XPS spectroscopy, the analyst is usually acquiring spectra over a large area from multiple positions on the sample and derives conclusions on “representative” chemical composition from average atomic concentrations and standard deviations. However, if lateral heterogeneities existing at the surface have smaller physical dimensions as the analysis area, the conclusions on “representative” chemical composition derived from large area spectroscopy will be erroneous. For accurate structural analysis of heterogeneous materials, it is very important to understand the scale of heterogeneity beforehand, so that the analysis areas and the size of the X-ray probe used for analysis are chosen appropriately. Often, complimentary microscopic techniques, such as SEM, are performed before XPS analysis which addresses some of this challenge but does not allow analysis over the same area.

The ability to perform small area spectroscopy for studying the heterogeneity and physical dimensions of samples is critical for obtaining accurate information on sample structure. In this talk, we will show examples of inaccurate use of large area spectroscopy and discuss the experimental approach towards selecting the relationship between the X-ray size and physical scale of defects and heterogeneities at the surface required to obtain an accurate representation of heterogeneous sample structure.

11:00am **AS+BI+RA-MoM9 Current Issues and Solutions for Reliable, Robust and Reproducible XPS Spectral Acquisition and Data Reporting**, *J.D.P. Counsell, C.J. Blomfield*, Kratos Analytical Limited, UK; **Christopher Moffitt**, Kratos Analytical Limited; *N. Gerrard, S.J. Coultas*, Kratos Analytical Limited, UK

XPS is now a truly interdisciplinary technique used in a wide variety of fields including catalysis, tribology, bioremediation and nuclear energy. With more than 1000 instruments currently in use, the ubiquitous nature of XPS means there is a greater requirement than ever for clarity regarding spectral acquisition, analysis and interpretation. The XPS user base has changed significantly – no longer the field of dedicated “technical experts” and spectroscopists – requiring instruments to be simple to use with a higher degree of automation in all parts of operation and analysis.

Here we will discuss the overall procedure for the technique specifying the critical steps in generating sound data and conclusions. Pitfalls and perils in the following steps will be briefly discussed: surface charging, beam damage, contamination, peak identification, energy calibration, quantification, peak-fitting, database usage, chemical state assignment and error reporting as will the latest methods implemented in mitigating against these issues. Worked examples and user studies will be presented to illustrate common inconsistencies.

11:20am **AS+BI+RA-MoM10 Intensity Calibration and Sensitivity Factors for XPS Instruments with Monochromatic Ag L α and Al K α Sources**, *A.G. Shard*, National Physical Laboratory, UK; *J.D.P. Counsell, Christopher Blomfield*, Kratos Analytical Limited, UK; *D.J.H. Cant*, National Physical Laboratory, UK; *E.F. Smith*, University of Nottingham, UK; *P. Navabpour*, Teer Coatings Ltd, UK

The use of monochromated Ag L α X-ray has been described previously.^{1,2} These sources have now become more widely available on commercial instruments and easier to use due to automation and the superior collection efficiency of modern analysers. To enable direct comparison between data acquired using both sources it is essential to be able have a common calibration scheme and a set of useful sensitivity factors. We employ the calibration method developed by the National Physical Laboratory for Al K α sources³ and extend this for Ag L α sources.⁴ Sensitivity factors for Ag L α and Al K α are calculated from photoionisation cross sections and electron effective attenuation lengths. These compare well to previous experimental values and data acquired from ionic liquids. The

intensity of the Ag L α source is found to be approximately 50 times lower than the Al K α source. This, coupled with generally lower photoemission efficiencies, results in noisier data or extended acquisition times. However, there are clear advantages to using the Ag L α source to analyse certain elements where additional core levels can be accessed and for many technologically important elements where interference from Auger electron peaks can be eliminated. The combination of calibrated data from both sources provides direct and easily interpreted insight into the depth distribution of chemical species. This could be particularly important for topographic samples, where angle resolved experiments are not always helpful. We also demonstrate, using thin coatings of chromium and carbon, that the inelastic background in Ag L α wide-scan spectra has a significantly increased information depth compared to Al K α .

References

1. Yates, K.; West, R. *Surf. Interface Anal.* **1983**,5 (4), 133-138.
2. Edgell, M.; Paynter, R.; Castle. *J. Electron Spectr. Rel. Phenom.* **1985**,37 (2), 241-256
3. Seah, M. P.. *J. Electron Spectr. Rel. Phenom.* **1995**,71 (3), 191-204.
4. Shard, A. G. *et al. Surf. Interface Anal.* **2019**<https://doi.org/10.1002/sia.6647>

11:40am **AS+BI+RA-MoM11 Reporting XPS Measurements and How Can We Do Better to Minimize Reproducibility Problems**, *Karen Gaskell*, University of Maryland, College Park

The level of detail and information provided in the average scientific article reporting XPS measurement and analysis varies widely. In some cases journal page limitations limit the inclusion of information such as experimental details, instrumental parameters and data sets that are required to fully describe the data collection and subsequent analysis so that it can be adequately reproduced by others. In other cases important information is simply left out. What are the minimum and preferable types of information we should include when reporting XPS results?

New Challenges to Reproducible Data and Analysis Focus Topic

Room A211 - Session RA+AS+NS+SS-MoA

Quantitative Surface Analysis II/Big Data, Theory and Reproducibility

Moderators: Kateryna Artyushkova, Physical Electronics, Donald Baer, Pacific Northwest National Laboratory

1:40pm **RA+AS+NS+SS-MoA1 A Data-Centric View of Reproducibility, Anne Plant**, National Institute of Standards and Technology (NIST); *J. Elliott*, NIST; *R. Hanisch*, National Institute of Standards and Technology (NIST)

INVITED

Ideally, data should be shareable, interpretable, and understandable within the scientific community. There are many challenges to achieving this, including the need for high quality documentation and a shared vocabulary. In addition, there is a push for rigor and reproducibility that is driven by a desire for confidence in research results. We suggest a framework for a systematic process, based on consensus principles of measurement science, to guide researchers and reviewers in assessing, documenting, and mitigating the sources of uncertainty in a study. All study results have associated ambiguities that are not always clarified by simply establishing reproducibility. By explicitly considering sources of uncertainty, noting aspects of the experimental system that are difficult to characterize quantitatively, and proposing alternative interpretations, the researcher provides information that enhances comparability and reproducibility.

2:20pm **RA+AS+NS+SS-MoA3 Enhancing Data Reliability, Accessibility and Sharing using Stealthy Approaches for Metadata Capture, Steven Wiley**, Pacific Northwest National Laboratory

INVITED

Science is entering a data-driven era that promises to accelerate scientific advances to meet pressing societal needs in medicine, manufacturing, clean energy and environmental management. However, to be usable in big data applications, scientific data must be linked to sufficient metadata (data about the data) to establish its identity, source, quality and reliability. This has also driven funding agencies to require projects to use community-based data standards that support the FAIR principles: Findable, Accessible, Interoperable, and Reusable. Current concerns about data reproducibility and reliability have further reinforced these requirements. Truly reusable data, however, requires an enormous amount of associated metadata, some which is very discipline and sample-specific. In addition, this metadata is typically distributed across multiple data storage modalities (e.g. lab notebooks, electronic spreadsheets, instrumentation software) and is frequently generated by different people. Assessing and consolidating all of the relevant metadata has traditionally been extremely complex and laborious, requiring highly trained and motivated investigators as well as specialized curators and data management systems. This high price has led to poorly documented datasets that can rarely be reused. To simplify metadata capture and thus increase the probability it will indeed be captured, EMSL (Environmental Molecular Sciences Laboratory) has developed a general-purpose metadata capture and management system built around the popular ISA-Tab standard (Investigation-Study-Assay Tables). We have modified this framework by mapping it onto the EMSL workflow, organized as a series of "transactions". These transactions are natural points where metadata is generated, include specifying how samples will be generated and shipped, instrument scheduling, sample storage, and data analysis. Software tools have been built to facilitate these transactions, automatically capture the associated metadata and link it to the relevant primary data. This metadata capture system works in concert with automated instrument data downloaders and is compatible with commercial sample tracking and inventory management systems. By creating value-added tools that are naturally integrated into the normal scientific workflow, our system enhances scientific productivity, thus incentivizing adoption and use. The entire system is designed to be general purpose and extensible and thus should be a useful paradigm for other scientific projects that can be organized around a transactional model.

3:00pm **RA+AS+NS+SS-MoA5 From Electrons to X-rays: Tackling Big Data Problems through AI, Mathew Cherukara, Y. Liu, M.V. Holt, H. Liu, T.E. Gage, J.G. Wen, I. Arslan**, Argonne National Laboratory

INVITED

As microscopy methods and detectors have advanced, the rates of data acquisition and the complexity of the acquired data have increased, and these are projected to increase several hundred-fold in the near future. The unique electron and X-ray imaging capabilities at the Center for Nanoscale Materials (CNM) are in a position to shed light on some of the most challenging and pressing scientific problems we face today. To fully leverage the capability of these advanced instruments, we need to design and develop effective strategies to tackle the problem of analyzing the data generated by these imaging tools, especially following facility upgrades such as the upgrade to the Advanced Photon Source (APS-U) and the commissioning of the ultrafast electron microscope (UEM).

The data problem is especially acute in the context of coherent imaging methods, ultra-fast imaging and multi-modal imaging techniques. However, analysis methods have not kept pace. It is infeasible for a human to sort through the large, complex data sets being generated from imaging experiments today. At the CNM, we apply machine learning algorithms to our suite of electron and X-ray microscopy tools. Machine learning workflows are being developed to sort through data in real-time to retain only relevant information, to invert coherently scattered data to real-space structure and strain, to automatically identify features of interest such as the presence of defects, and even to automate decision making during an imaging experiment. Such methods have the potential not only to decrease the analysis burden on the scientist, but to also increase the effectiveness of the instruments, for instance by providing real-time experimental feedback to help guide the experiment.

4:00pm **RA+AS+NS+SS-MoA8 Quantifying Shell Thicknesses of Core-Shell Nanoparticles by means of X-ray Photoelectron Spectroscopy, Wolfgang Werner**, Vienna University of Technology, Austria

INVITED

Determining shell thicknesses and chemistry of Core-Shell Nanoparticles (CSNPs) presently constitutes one of the most important challenges related to characterisation of nanoparticles. While for particulae number concentration various routine analysis techniques as well as methods providing reference measurements have been or are in the process of being developed, one of the most promising candidates for shell thickness determination is x-ray photoelectron spectroscopy (XPS).

Different approaches to quantify shell thicknesses will be presented and compared. These comprise: (1) The infinitesimal columns model (IC), (2) Shard's empirical formula (TNP-model) and (3) SESSA (Simulation of Electron Spectra for Surface Analysis) simulations with and (4) without elastic scattering.

CSNP XPS intensities simulated with SESSA for different combinations of core/shell-material combinations for a wide range of core and shell thicknesses have been evaluated with the TNP-model and the retrieved thicknesses are in good agreement with the nominal thickness, even when elastic scattering is turned on during the simulation, except for pathological cases. For organic shell materials these simulations fully confirm the validity of the (much simpler) TNP-method, which also coincides with the IC model.

Experimental data on of a round robin experiment of PMMA@PTFE CSNPs involving three research institutions were analysed with the aforementioned approaches and show a good consistency in that evaluations of the shell thicknesses among the institutions agree within 10% (and are in good agreement with the nominal shell thickness). This consistency is promising since it suggests that the error due to sample preparation can be controlled by following a strict protocol.

Use of the F1s signal leads to significant deviations in the retrieved shell thickness. Independent measurements using Transmission Electron Microscopy were also performed, which revealed that the core-shell structure is non-ideal, i.e. the particles are aspherical and the cores are acentric within the particles. SESSA simulations were employed to estimate the effect of various types of deviations of ideal NPs on the outcome of shell thickness determination.

The usefulness and importance of different kind of electron beam techniques for CSNP analysis and in particular shell thickness determination is discussed.

4:40pm **RA+AS+NS+SS-MoA10 Modeling the Inelastic Background in X-ray Photoemission Spectra for Finite Thickness Films**, *Alberto Herrera-Gomez*, CINVESTAV-Unidad Queretaro, México

The background signal in photoemission spectra caused by inelastic scattering is usually calculated by convolving the total signal with the electron-energy loss-function. This method, which was proposed by Tougaard and Sigmund in their classic 1982 paper [1], only works (as clearly indicated in [1]) for homogeneous materials. However, the method is commonly applied to finite thickness films. In this paper it is going to be described the proper way to remove the inelastic background signal of spectra from thin-conformal layers including buried layers and delta-doping [2]. The method is based on the straight-line inelastic scattering path, which is expected to be a very good approximation for low energy losses (near-peak regime). It is also a common practice to use the parametric Tougaard Universal Cross Section [3] with the provision that, instead of using the theoretical values for the parameters valid for homogeneous materials, the B-parameter is allowed to vary until the experimental background signal ~ 50 to 100 eV below the peak is reproduced. This is equivalent to scale the loss-function, which partially compensates the error from using the convolution method [1]. The error compensation on the modeling of the background of finite-thickness layers by scaling the loss-function will be quantitatively described.

[1] S. Tougaard, P. Sigmund, Influence of elastic and inelastic scattering on energy spectra of electrons emitted from solids, *Phys. Rev. B.* 25 (1982) 4452–4466. doi:10.1103/PhysRevB.25.4452.

[2] A. Herrera-Gomez, The photoemission background signal due to inelastic scattering in conformal thin layers (Internal Report), 2019. http://www.qro.cinvestav.mx/~aherrera/reportesInternos/inelastic_background_thin_film.pdf.

[3] S. Tougaard, Universality Classes of Inelastic Electron Scattering Cross-sections, *Surf. Interface Anal.* 25 (1997) 137–154. doi:10.1002/(SICI)1096-9918(199703)25:3<137::AID-SIA230>3.0.CO;2-L.

5:00pm **RA+AS+NS+SS-MoA11 R2R(Raw-to-Repository) Characterization Data Conversion for Reproducible and Repeatable Measurements**, *Mineharu Suzuki, H. Nagao, H. Shinotsuka*, National Institute for Materials Science (NIMS), Japan; *K. Watanabe*, ULVAC-PHI Inc., Japan; *A. Sasaki*, Rigaku Corp., Japan; *A. Matsuda, K. Kimoto, H. Yoshikawa*, National Institute for Materials Science (NIMS), Japan

NIMS, Japan, has been developing a materials data platform linked with a materials data repository system for rapid new material searching by materials informatics. The data conversion from raw data to human-legible/machine-readable data file is one of the key preparation techniques prior to data analysis, where the converted data file should include meta-information. Our tools can convert raw data to a structured data package that consists of (1) characterization measurement metadata, (2) primary parameters which we will not call “metadata” to distinguish from (1), (3) raw parameters as written in original raw data, and (4) formatted numerical data. The formatted numerical data are expressed as matrix type with robust flexibility, not obeying a rigid definition. This flexibility can be realized by applying the data conversion style of Schema-on-Read type, not Schema-on-Write type based on *de jure* standards such as ISO documents. The primary parameters are carefully selected from raw parameters and their vocabularies are replaced from instrument-dependent terms to general ones that everyone can readily understand. These primary parameters with linked specimen information are useful for reproducible and repeatable instrument setup. By this R2R conversion flow, we have verified that we can generate and store interoperable data files of XPS spectra and depth profiles, powder XRD patterns, (S)TEM images, TED patterns, EELS spectra, AES spectra, EPMA spectra and elemental mapping, and theoretical electron IMFP data. We have also developed a system to allow semi-automatic data transfer from an instrument-controlling PC isolated from the network, by adopting a Wi-Fi-capable SD card’s scripting capability, while keeping the PC offline. We are working on further software development for on-demand data manipulation after R2R data conversion. So far it has been possible to perform XPS peak separation using automated information compression technique. Using these components, high-throughput data conversion/accumulation and data analyses are realized, where human interaction is minimized. Using metadata extracted from raw data, other users can reproduce or repeat measurements even if they did not carry out the original measurement. Human-legible and machine-readable numerical data is utilized for statistical analyses in informatics.

Applied Surface Science Division

Room A211 - Session AS+BI+RA-TuM

Quantitative Surface Analysis III/Other Surface Analysis Methods

Moderator: Karen Gaskell, University of Maryland, College Park

8:00am **AS+BI+RA-TuM1 Oxygen Energy Filtering and Relative Sensitivity Factor Considerations for Making U and Pu Measurements by LG-SIMS, Todd Williamson**, Los Alamos National Laboratory **INVITED**

During nuclear facility inspections, inspectors collect materials intended to show a history of the operations that have taken place within a facility.

These materials can be particles obtained using cotton swipes, solid discarded or operationally related nuclear materials, or other items contaminated with nuclear materials. Analysis of these samples is an extremely powerful tool with which to determine facility operations and history. Uranium analysis by SIMS is a mature technique used by the IAEA and its Network of Analytical Laboratories for treaty verification. The analysis of mixed uranium-plutonium particles and solids is not as mature as a capability and has been identified by the IAEA as topic for increased R&D.

This presentation will cover two technical topics related to the analysis of mixed uranium-plutonium materials, relative sensitivity factors (RSF) and energy filtering to improve hydride correction. For a material that contains both U and Pu, while both elements will be sputtered and become ionized during SIMS analysis, they will do so with different efficiencies. This ionization difference tends to be sample-type (matrix) dependent. This phenomenon is known as the relative sensitivity factor (RSF). This presentation will discuss our investigations into determining accurate RSF values for U:Pu and U:Np inter-element measurements. With accurate RSF values, which should be universal for a given sample type, the measured inter-isotope ratios can be corrected to their true values. In a mixed actinide sample, there is ^{239}Pu present which will be unresolvable from $^{238}\text{U}^+\text{H}$. This will prevent a conventional hydride correction on measurements, and there are not other clean masses in a mixed actinide sample where a hydride signal can be easily measured. Without a hydride correction the measurement of smaller concentration isotopes will have poor accuracy due to interference from large hydride interferences from major isotopes, and ^{239}Pu measurements will be highly inaccurate. The presentation will discuss our use of energy filtering mediated by an intentionally introduced partial pressure of oxygen in the sample analysis chamber, which changes ionization behavior.

8:40am **AS+BI+RA-TuM3 Utilizing Large Geometry Secondary Ion Mass Spectrometry for Age-Dating of Individual Uranium Particles, Christopher Szakal, D.S. Simons, J.D. Fassett**, National Institute of Standards and Technology (NIST); *A.J. Fahey*, Corning Inc.

Secondary ion mass spectrometry (SIMS) is routinely utilized by the International Atomic Energy Agency (IAEA) and its global partner laboratories for the isotopic analysis of individual uranium particles as part of nuclear safeguards efforts. One additional isotopic analysis that has repeatedly been requested by the IAEA involves the development of a capability to perform single particle age-dating, which would provide information about the last time that the nuclear material was purified or enriched. Previously reported efforts in multiple countries have reported the ability to use SIMS and/or large geometry (LG)-SIMS for this purpose, but with the caveat that the measurement can only be viable if the particles are large enough, old enough, and/or enriched enough. We present a new methodology, complete with propagated uncertainties, that advances the individual uranium particle age-dating measurement to include smaller, younger, and lower enriched nuclear material than previously envisioned. Additionally, we will provide insights into utility of this measurement advance within the aims of global nuclear safeguards objectives.

9:00am **AS+BI+RA-TuM4 Peak Shape Analysis in TOF SIMS: Best Practices and Limiting Precision in Accounting for Detector Saturation, Lev Gelb, A.V. Walker**, University of Texas at Dallas

We compare strategies for analyzing high-mass resolution TOF SIMS data sets affected by detector saturation. The detectors used in many instruments undercount ions due to saturation effects. If two or more ions arrive within a very short interval (the "dead time") only the first ion is recorded. This changes both the total number of ions collected and their

statistical distribution. The dead time is typically short enough that only ions of the same nominal mass are affected, but a significant fraction of the total ions reaching the detector may still be missed.

We demonstrate an approach to correct for dead time errors in which a probability model for the detector behavior is developed and used in peak fitting of the "uncorrected" data. This approach has many advantages over previous methods which required an estimate of the variance, and it behaves better under conditions of poor data quality (low counts or high saturation.)

Using both synthetic and experimental data, we examine how saturation affects apparent peak shape, position and intensity, the effects of background on estimated peak position and shape, the dependence of peak-location precision on the total number of counts, how interference between satellite peaks is best accounted for, and the biases exhibited by different data analyses. Finally, we extend these methods to imaging data taken at high mass resolution and compare the results obtained with analyses performed at unit-mass resolution.

9:20am **AS+BI+RA-TuM5 Electronic Structure and Band Gaps of Industrially Relevant Materials Investigated by Photoelectron Spectroscopy and REELS (Reflection Electron Energy Loss Spectroscopy), Paul Mack, T.S. Nunney**, Thermo Fisher Scientific, UK; *H.M. Meyer III*, Oak Ridge National Laboratory

Many inorganic and organic materials have been created and evaluated for use in a diverse range of applications, such as microelectronics, solar cells and TV displays. The electronic properties of these materials can be tuned by modifying their elemental or chemical state composition. Ideally, the analyst would like to characterize both the composition and electronic properties of a given material in a single experimental run, enabling correlation between electronic properties and composition to be established.

In this work thin films of industrially relevant materials, such as polydiocetylfluorene, which is a polymer light emitting diode (PLED), and HfO_2 were analysed using a multi-modal approach. (Thermo Scientific ESCALAB Xi+ and Nexsa tools, configured with multiple surface analysis techniques, were used for the analysis.)

X-ray photoelectron spectroscopy was used to measure elemental and chemical state composition (together with some electronic information) and ultraviolet photoelectron spectroscopy was used to measure ionization potentials and the energies of the highest occupied molecular orbitals (HOMOs). Information about the band gap and lowest unoccupied levels (LUMOs), which cannot be determined with XPS or UPS, was measured with REELS. Energy level diagrams for the materials could then be constructed using the information from the complementary spectroscopic techniques.

Due to the low kinetic energy of photoelectrons generated by the ultraviolet source, UPS is a particularly surface sensitive spectroscopy. When analyzing samples stored in the atmosphere, the resulting data is typically dominated by surface adventitious carbon. This carbon needs to be removed, but with care not to damage the underlying material being studied. The use of an argon cluster ion beam for this kind of careful sample preparation was demonstrated in this work.

9:40am **AS+BI+RA-TuM6 Practical References for Low Energy Ion Scattering by Ca and F, S. Průša, T. Šikola**, Brno University of Technology, Czech Republic; *Hilde Brongersma*, IONTOF Technologies GmbH, Germany/Eindhoven University of Technology, Eindhoven, The Netherlands, Germany

Low-Energy Ion Scattering (LEIS) is known for its extreme surface sensitivity. It is just as well suited for the analysis of amorphous, isolating, extremely rough surfaces, as for flat single crystals. Thus LEIS is applicable to any type of sample that can be taken into vacuum. Since matrix effects are generally absent, or relatively small in LEIS, a quantitative analysis is straightforward. However, the theory to quantitatively predict the atomic sensitivities of the elements falls short. Therefore, an accurate quantification relies on well-defined reference materials. Practical references should be chemically inert, easy to clean and inexpensive. The powder of calcium fluoride, CaF_2 , has been suggested as practical reference for Ca and F [1], while the powder of calcium carbonate, CaCO_3 , has also been suggested for Ca [2].

A complication is that the composition of the outer atomic layer of a material is generally fundamentally and radically different from that of the atoms below this surface. Thus it is unlikely that the F/Ca ratio in the outer surface of CaF_2 will be 2. In fact, precisely this difference makes the LEIS

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information unique and complementary to that of analytic techniques such as XPS, Auger and (TOF-) SIMS which probe several to many atoms deep. The difference is also highly relevant, since the outer atoms of a surface largely control important processes as adhesion, catalysis, electron emission and growth

It will be shown how the F/Ca atomic ratio, the Ca and F atomic densities, as well as the roughness factors for CaF₂ and CaCO₃ have been determined.

[1] T. Gholian Avval, C.V. Cushman, P. Br uner, T. Grehl, H.H. Brongersma, M.R. Linford,

Surf. Sci. Spectra, to be published (2019)

[2] R.M. Almeida, R. Hickey, H. Jain, C.G. Pantano, J. Non-Cryst. Solids 385 (2014) 124

11:00am **AS+BI+RA-TuM10 Extreme-Ultraviolet-Assisted Atom Probe Tomography**, *Norman Sanford*, *L. Miaja Avila*, National Institute of Standards and Technology (NIST); *P. Blanchard*, National Institute of Standards and Technology (NIST); *D.R. Diercks*, *B. Gorman*, Colorado School of Mines; *A. Chiaramonti*, National Institute of Standards and Technology (NIST)

Laser-assisted atom probe tomography (L-APT) often returns compositional biases that deviate from a specimen's true chemical makeup [1]. In our L-APT studies of GaN, which utilize a 355 nm laser, we find stoichiometric composition (50% Ga, 50% N) only when the pulse fluence is roughly 2E-7 J/cm². Higher fluences return nonphysical, Ga-rich compositions; lower fluences give nonphysical N-rich compositions. L-APT of other materials, including SiO₂, exhibit similar biases. L-APT is a thermally-activated mechanism. The specimen is subjected to a strong electric field that is held just below the threshold for field evaporation of ions; evaporation is triggered by thermal transients imparted by the incident laser pulses. Motivated by the need to improve the quantitative accuracy of atom probe tomography, we explored an alternative, photoionization-triggered pathway for field evaporation by replacing the conventional laser on an L-APT tool with a pulsed, extreme-ultraviolet (EUV) source—thus realizing the XAPT [2,3]. The tabletop EUV source is an ultrafast, amplified Ti:sapphire laser driving an Ar-filled capillary waveguide. Pulsed, coherent EUV is produced via high-harmonic generation [4]. The respective characteristics of EUV pulse width, repetition rate, wavelength (energy), and fluence, incident on a specimen tip are: 10 fs, 10 kHz, 30 nm (42 eV), and 2.5E-8 J/cm². Comparative XAPT and L-APT analyses were performed on specimens of GaN and SiO₂ (amorphous fused silica). For SiO₂, L-APT returned an off-stoichiometry composition of 41% Si and 59% O; XAPT yielded 33% Si and 66% O (stoichiometry). For GaN, XAPT found 49% Ga and 51% N; L-APT yielded laser-pulse-fluence-dependent composition and returned 68% Ga and 32% N for a fluence of roughly 2E-6 J/cm²; L-APT conditions giving stoichiometric GaN appear above. The uncertainty of these measurements is 1–3 at. %. All specimens were examined at 50 K. XAPT-derived mass spectra show reduced occurrences of molecular ions and reduced “thermal tails” (persistent field emission following the laser pulse). Ongoing work for presentation at the meeting includes comparative studies of InGaN, Mg:GaN, and AlGaN. In all cases examined thus far, the XAPT approach offers measurable improvements over L-APT.

1. D. J. Larson, et al, Local Electrode Atom Probe Tomography (Springer, New York, 2013)

2. A. N. Chiaramonti, et al, MRS Advances (in press, 2019)

3. L. Miaja Avila, et al, Frontiers in Optic (FiO), Optical Society of America, Wash. DC, p. FTu5C. 3 (2018)

4. L. Miaja Avila, et al, Phys. Rev. Lett. 97, 113604 (2006)

11:20am **AS+BI+RA-TuM11 A Multi-Technique Approach for Complete Thin Film Characterisation**, *Sarah Coultas*, *J.D.P. Counsell*, *N. Gerrard*, *C.J. Blomfield*, Kratos Analytical Limited, UK; *C. Moffitt*, Kratos Analytical Limited; *T. Conard*, IMEC, Belgium

The application of thin film technology is of commercial importance across a range of industries and is commonly used to influence both the physical and chemical properties of bulk materials. Ranging in thickness from tens of Angstroms to microns, their applications are used across a broad range of disciplines including the semiconductor, biomaterial and energy harvesting industries. Herein, we provide a multi-technique investigation of layered thin film and ultra-thin film coatings using a model system for gate oxide structures. The combination of techniques allows one to build a complete picture of the chemistry of these materials and how subtle differences in chemistry and stoichiometry can influence the properties of a substrate to enhance its application specificity.

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the surface chemistry of these layered thin film materials. Using monochromated Al-K α (1486.6 eV) X-rays, it was possible to gain quantitative chemical information from the uppermost 10 nm of the surface. In this study, we illustrate how angle-resolved XPS (ARXPS) can be used as a more surface sensitive approach to probe only the topmost 1-3 nm, and how one can utilize maximum entropy modelling (MEMS) to recreate a concentration depth profile from the resulting data.

In contrast to increased surface sensitivity, high energy excitation sources can be used to extend the analysis depth of a material to >15 nm. Here, we describe the use of a monochromated Ag-L α (2984.2 eV) X-rays to delve deeper into the bulk structure. In combination with ARXPS, the greater excitation energy and increased analysis depth allows one to measure elemental core levels which are not accessible using the conventional Al-K α source. In light of this, one can build a more detailed description of the structure of these thin film materials and their use in relevant applications.

11:40am **AS+BI+RA-TuM12 Polymeric Barrier Coatings for Silicone Elastomer against Diffusion of Isocyanate in Vacuum Casting Processes**, *Martin Wortmann*, *R. Petkau*, Bielefeld University of Applied Sciences, Germany; *N. Frese*, Bielefeld University, Germany; *E. Moritzer*, Paderborn University, Germany; *A. G lzh user*, Bielefeld University, Germany; *B. H usgen*, Bielefeld University of Applied Sciences, Germany

The vacuum casting process is used industrially to replicate prototypes of polyurethane (PUR). Due to the diffusion of 4,4'-methylene diphenyl diisocyanate (MDI), a PUR resin component, the silicone casting molds used in this process show a progressive degradation, which leads to the failure of the casting molds after a few casting cycles [1]. In this contribution, we present ways to protect the surface of the silicone elastomer by various thermoplastic polymer coatings. The polymers investigated were dissolved in different volatile solvents and coated on pretreated silicone surfaces. For this purpose, the compatibility of those polymer solutions with polydimethylsiloxane (PDMS) was investigated and their diffusion coefficients with respect to MDI were measured. Polymer coatings that have exhibited a high diffusion barrier have been used to drastically increase the output of the casting molds.

[1] M. Wortmann et al., *Polymer Plast Tech Eng* 57, 1524 (2018).

12:00pm **AS+BI+RA-TuM13 pARXPS Study of GeSbTe Surface Oxidation**, *Ludovic Goffart*, ST Microelectronics/LTM/CEA-LETI, France; *C. Vall e*, Laboratoire des Technologies de la Micro lectronique (LTM), France; *B. Pelissier*, LTM, Univ. Grenoble Alpes, CEA-LETI, France; *J.-P. Reynard*, *D. Benoit*, ST Microelectronics, France; *G. Navarro*, CEA-LETI, France

This work is focusing on the oxidation of the well-known GST material (Ge₂Sb₂Te₅, GST225) widely used in storage optics like CD, DVD and Blu-ray. This time, we use the GST for its electrical properties to create a non-volatile memory. The GST we use in this work is modified from the GST225 chemical composition to comply with the specifications needed in automotive applications, the most important being a good stability and cycling at high temperature environment.

This non stoichiometric GST composition leads to instability in its structure, therefore more aging and oxidation which conflict with the objectives of this new PCM cell. Added to this is some atomic segregation during crystallographic relaxation, which leads to low cycling durability of the cell and lower crystallization temperatures. To counter these effects, the GST material is doped but this makes more complex the chemical characterization of the material.

To understand and overcome these problems, different GST materials (from 225 to Ge rich) have been characterized using the pARXPS technique which is an angular resolved XPS. With this technique a very complete chemical characterization of the surface of these samples have been performed to gather useful information of atomic segregations and surface oxidation, by acquiring 8 simultaneous angles at the same time for different element windows. This is only possible by developing a complex fitting model for the large amount of spectra obtained. This model has to deal with the complex feature of the spectra obtained since some peaks were overlapping. Physical constraints are then necessary to obtain a realistic fit of the spectra. Once the model optimized, the aging of the samples have been studied by monitoring the evolution of specific XPS shapes with time. As a result, the oxidation kinetic and the thickness of the oxidized surfaces are quantified and finally a depth profile reconstruction of the different chemical bonds is performed. In addition to pARXPS, TEM-EDX analysis were performed to confirm the fitting model developed and profile depth reconstruction obtained with pARXPS technique.

New Challenges to Reproducible Data and Analysis Focus Topic

Room A124-125 - Session RA+AS+CA+PS+TF-WeM

Reproducibility in Science and Engineering, Including Materials and Energy Systems

Moderators: Karen Gaskell, University of Maryland, College Park, Svitlana Pylypenko, Colorado School of Mines

8:00am **RA+AS+CA+PS+TF-WeM1 Reproducibility and Replicability in Science and Engineering: a Report by the National Academies, Dianne Chong**, Boeing Research and Technology (Retired) **INVITED**

One of the pathways by which scientists confirm the validity of a new finding or discovery is by repeating the research that produced it. When a scientific effort fails to independently confirm the computations or results of a previous study, some argue that the observed inconsistency may be an important precursor to new discovery while others fear it may be a symptom of a lack of rigor in science. When a newly reported scientific study has far-reaching implications for science or a major, potential impact on the public, the question of its reliability takes on heightened importance. Concerns over reproducibility and replicability have been expressed in both scientific and popular media.

As these concerns increased in recent years, Congress directed the National Science Foundation to contract with the National Academies of Science, Engineering, and Medicine to undertake a study to assess reproducibility and replicability in scientific and engineering research and to provide findings and recommendations for improving rigor and transparency in research.

The committee appointed by the National Academies to carry out this task included individuals representing a wide range of expertise: methodology and statistics, philosophy of science, science communication, behavioral and social sciences, earth and life sciences, physical sciences, computational science, engineering, academic leadership, journal editors, and industry expertise in quality control. Individuals with expertise pertaining to reproducibility and replicability of research results across a variety of fields were included as well.

This presentation will discuss the committee's approach to the task and its findings, conclusions, and recommendations related to factors that influence reproducibility, sources of replicability, strategies for supporting reproducibility and replicability, and how reproducibility and replicability fit into the broader framework of scientific quality and rigor.

8:40am **RA+AS+CA+PS+TF-WeM3 Directly Assessing Reproducibility in Materials Chemistry Research Using Literature Meta-analysis, David Sholl**, Georgia Institute of Technology **INVITED**

While it is widely agreed that making reported research more reproducible is a desirable goal, less is known about how reproducible current work in materials chemistry is. I will discuss using literature meta-analysis as a tool to obtain quantitative insight into the reproducibility of materials chemistry experiments. Case studies will be discussed involving measurements of gas adsorption in metal-organic frameworks and the synthesis of metal-organic framework materials. These are useful examples to study because comprehensive databases of information from the open literature are available, but they share features that are common in many areas of material chemistry. Insights from these case studies suggest possible paths towards improving data reproducibility for individual researchers, for academic departments and for professional organizations.

9:20am **RA+AS+CA+PS+TF-WeM5 Reproducibility in Fundamental and Applied Science, George Crabtree**, Argonne National Laboratory, University of Illinois at Chicago **INVITED**

The scientific enterprise operates via a few basic features, including questions, insight, hypotheses, critique, reproducibility, elaboration and revision. All contribute to the process of discovery, none can be taken as the single signature of scientific truth. Discovery science is a dynamic process informed by new observations and continuous refinement of the precision, accuracy, principals and scope of our collective scientific knowledge. History has many examples of significant revisions of previously accepted dogma based on new observations (the earth is flat, matter is infinitely divisible, the stars are fixed). New insights lead to new fundamental principles (energy is conserved, nothing can go faster than light, germs cause disease) that open new opportunities for advancing the scientific frontier and raising the quality of life. Examples of advances of the
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frontiers of energy science and their implications for reproducibility will be given.

11:00am **RA+AS+CA+PS+TF-WeM10 Representativeness of a TEM image for Revealing New Phenomenon in Energy Storage Materials, Chongmin Wang**, Pacific Northwest National Laboratory; *D.R. Baer*, Pacific Northwest National Laboratory

Transmission electron microscopy (TEM), as a imaging technique with high spatial resolution, appears to be a routine tool for showcasing, often viewed as an enlightening figure, the structural and chemical information of materials at multiscale of down to single atomic column. One of a very common questions that raised by the viewer, not necessarily suspicious, is the representativeness of the image to the real situation as considering the sampling scale of the TEM imaging method. This question is further elevated for the case of in-situ and operando observation as which naturally couples in another dimension of "time" in addition to the "spatial" scale. In addition, beam effect can be coupled in for artifacts. In this presentation, we will check into the reproducibility of TEM imaging of both in-situ and ex-situ for revealing new phenomenon in energy storage materials, while certain cautions may also be necessary for interpreting new observations based on TEM.

11:20am **RA+AS+CA+PS+TF-WeM11 Reproducibility Issues when Developing Catalysts for Fuel Cell Applications, M.J. Dzara, S.F. Zaccarine**, Colorado School of Mines; *K. Artyushkova*, Physical Electronics and University of New Mexico; *Svitlana Pylypenko*, Colorado School of Mines

This talk will discuss reproducibility issues encountered during the development of novel catalysts for low temperature fuel cell performance (PEMFC) as replacements of state-of-the-art catalysts that contain Pt-based nanoparticles supported on a high surface area carbon support. Examples across several catalytic systems will be shown, including low platinum-group metal (low-PGM) catalysts with extended surfaces derived from nanowire templates, and PGM-free catalysts based on N-doped carbon with an atomically dispersed transition metal.

Reproducibility issues related to the synthesis of these catalytic materials and their impact on the performance of these catalysts will be reported first following by discussion of challenges in characterization. Specifically, the need for complementary characterization will be highlighted along with issues that arise when materials are characterized by different groups using different techniques. Another set of reproducibility issues arises when conducting characterization of catalysts under in-situ and in-operando conditions.^[1] The time constraints imposed by the availability of instrumentation result in datasets that have a limited number of samples, areas per samples and replicate measurements on the same sample.

(1) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas – Solid Interface with in Situ Spectroscopy : The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C* **2019**, *123* (14), 9074–9086.

11:40am **RA+AS+CA+PS+TF-WeM12 Challenges in Multimodal Spectroscopic Analysis of Energy Storage Materials, Vijayakumar Murugesan**, Pacific Northwest National Laboratory; *K.T. Mueller*, Joint Center for Energy Storage Research (JCESR) **INVITED**

Charge transfer across heterogeneous interfaces facilitated by redox reactions is the basis of energy storage technology. Capturing the interfacial processes over broad scales both spatially (ranging from angstroms up to 100 nm) and temporally (lasting from fs up to a few minutes) is a major challenge. This is one origin of the existing knowledge gaps in energy storage materials, which impede our ability to predict and control the emergent behaviors at electrochemical interfaces. As part of Joint Center for Energy Storage Research (JCESR) center, we developed a multi-modal in situ characterization tool set based on X-ray absorption, photoelectron and multinuclear NMR spectroscopy in combination with computational modelling that can access a range of the important complex processes. This multimodal approach helps us gain critical insights of the charge transfer process, but also presented unique challenges in data collection, analysis and reproducibility. The multitude of constituents and varying surface chemistry combined with external stimuli (applied potential and temperature) challenges the traditionally conceived time and spatial resolution limitations of the probes. For example, establishing reference systems and base line measurements for electrochemical process where combinatorial constituents react and depend on the charge state is a major challenge in spectroscopic studies and complicates subsequent corroboration with computational analysis. In this talk, we will discuss overcoming these challenges and apply the methods to critically analyzing

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solid-electrolyte interphase (SEI) evolution in Li-metal based batteries,
multivalent ion transport across membranes and chemical stability of redox
flow battery electrolytes.

New Challenges to Reproducible Data and Analysis Focus Topic

Room A124-125 - Session RA+AS+BI-WeA

Addressing Reproducibility Challenges using Multi-Technique Approaches

Moderators: Tony Ohlhausen, Sandia National Laboratory, Vincent Smentkowski, GE-Research

2:20pm **RA+AS+BI-WeA1 Responding to New and Old Challenges to Data, Analysis and Scientific Study Reproducibility, Donald Baer**, Pacific Northwest National Laboratory; *I.S. Gilmore*, National Physical Laboratory, UK

An increasing number of studies, surveys and editorials highlight experimental and computational reproducibility and replication issues that frequently appear in most areas of modern science. In a 2018 AVS conducted survey, 66% of those responding identified reproducibility as a significant issue. There are multiple and complex causes of what some have called a "reproducibility crisis," which can impact materials, interface/(bio)interphase, vacuum and others sciences of importance to AVS members. Reproducibility challenges are not new, but now appear in both old and new forms requiring innovative solutions. Drivers influencing reproducibility problems include the increasingly multi-discipline, multi-method nature of much advanced science, increased complexity of the problems and systems being addressed, and the large amounts and multiple types of experimental and computational data being collected and analyzed in many studies. Such issues challenge experimental teams and the review process. Systematic and sustained efforts are needed to address the causes of reproducibility problems that can hinder the rate of scientific progress and lower public and political regard for science. The Focus topic New Challenges to Reproducible Data and Analysis aims to raise awareness of the challenges, examine the causes, impacts of reproducibility problems and explore approaches that can help address both the newer and older generation of reproducibility challenges. Some problems and solutions are easy to identify, even if not readily implemented. Other drivers and causes are less obvious and therefore harder to address. This talk will introduce the focus topic sessions, review key literature on the topic of reproducibility and summarize how the presentations fit together as a way to address reproducibility challenges.

2:40pm **RA+AS+BI-WeA2 Achieving Reproducible Data: Examples from Surface Analysis in Semiconductor Technology, Thierry Conard, P.A.W. van der Heide, A. Vanleenhove, C. Zborowski, W. Vandervorst**, IMEC, Belgium

Repeatability and reproducibility in surface analysis in the semiconductor industry are key to for supporting efficient process development as well as High Volume Manufacturing (HVM). As two examples, long term repeatability is critically important when comparing to historical data, while reproducibility is required to support technology transfers when HVM of specific devices is to be carried out at multiple sites. This however introduced a number of unique challenges for running a characterization facility.

In this presentation we will present a number of examples that can result in reproducibility issues. Particular focus will be in the areas of X-ray Photoelectron Spectroscopy (XPS) Secondary Ion Mass Spectrometry (SIMS). The first and foremost causes of repeatability and reproducibility arise from instrumental variation. A second important source arises from samples variability. We will show that assessing long-term instrumental stability is potentially hindered by long term variation of samples characteristics. We will also show that an understanding of the characterization techniques is paramount to understanding such issues.

Next to the "pure" technical causes of repeatability and reproducibility, is the human factor. This involve for instance decision making in data treatment during for example, fitting procedures, statistical treatments, etc. This will be illustrated using practical examples. And with present day characterization depending more heavily on computational support/commercial software, potential detriments to characterization repeatability will again be made evident. Finally, we will show through round-robin results, that combining all the above factors, widely varying results can be obtained on the same samples.

3:00pm **RA+AS+BI-WeA3 New Challenges in Analytical Reproducibility Illustrated with Old and New Case Studies, Thomas Beebe Jr**, University of Delaware

INVITED

To address the subject of this session's topic, "New Challenges to Reproducible Data and Analysis," I have chosen to select a few case studies from my research group's work over the past 30 years. My examples will therefore be drawn from the methods and techniques that I have employed: XPS, TOF-SIMS, AFM, STM, and from the surface-related fields in which we have worked: biomolecules on surfaces, molecular self-assembly, biomaterials, and perhaps some others. It has always been my goal and approach to employ careful controls, scientific statistics, and data extraction to the richest extent possible.

4:20pm **RA+AS+BI-WeA7 Challenges and Approaches to Addressing Reproducibility in Biointerface Science and Engineering, Sally McArthur**, Swinburne University of Technology and CSIRO, Australia, Australia

INVITED

Our publications should serve as guides to repeat our experiments/analyses and reproduce the results; however, quite often we may find ourselves not able to do so. Over the past few years, there have been many papers and editorials that have shown that issues associated with Repeatability, Reproducibility, and Replicability impact almost all areas of science, and in an AVS-conducted survey, 65% of those responding indicated that they have seen or experienced significant reproducibility issues when they have sought to recreate experiments from the literature. It is clear that the increasing demands of complex research requiring use of multiple experimental and computational research methods is a central theme. The challenge in the Biointerface Science community is compounded by the inherent variability of biology. Working at the interface between the physical and life sciences, it is often difficult for us to have in-depth knowledge of the idiosyncrasies of the many techniques we use and we need to be aware of for our data interpretation. This talk will discuss approaches we are taking to tackle this issue within the Biointerface Science Community and the journal Biointerphases. We will look at how we can champion best practices, sharing our knowledge across our community, and seek to support researchers who are new to the field or want to explore new techniques to avoid the pitfalls and better understand both the opportunities and limitations of the techniques, methods, and approaches used in our multidisciplinary community.

Sally L McArthur, Editor Biointerphases

5:00pm **RA+AS+BI-WeA9 Complementary Measurements of Colloidal Nanoparticles and their Coatings by In-situ and Vacuum-based Methods, Caterina Minelli**, National Physical Laboratory, UK

INVITED

Engineered nanoparticles add high value to commercial products and have the potential to improve our quality of lives and boost prosperity. For example, they provide radical new approaches to cancer drug delivery, biosensing, medical imaging and catalysis. However, the effective implementation of these materials relies on the ability to measure and control their properties, such as their surface chemical identity, size and concentration. There are significant challenges in the analysis of nanomaterials due to, among other factors, the interdisciplinary nature of the field and the lack of adequate reference materials to calibrate analytical tools. The use of complementary tools provides opportunities for (1) deepening the quantitative understanding of these systems and, importantly, (2) a route to method validation. I will provide examples from our work on both these cases.

(1) We use a combination of methods to analyse nanoparticles which are employed in liquid media (*in-situ*) using techniques such as analytical centrifugation and dynamic light scattering and *ex-situ* with X-ray photoelectron spectroscopy (XPS). Sound sample preparation protocols are critical for meaningful and comparable measurements. This is especially important when using complementary methods for the analysis of the same samples. I will discuss our experience in the analysis of protein coated gold nanoparticles and polymeric core/shell nanoparticles and show how multimodal analysis is critical to the full understanding of the system.

(2) The lack of certified reference materials for nanoparticle number concentration has hindered the validation of laboratory methods, which resulted in a general distrust in commercially available instrumentation. We have led a collaborative effort to develop accurate methods based on small angle X-ray scattering (SAXS) and single particle inductively coupled plasma mass spectrometry (spICPMS) for the measurement of colloidal number concentration. We have then used these methods to assess and validate a range of laboratory methods. I will discuss the result of this work for both ideal and agglomerated nanoparticles and present the outcomes

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of a large VAMAS interlaboratory study which assessed four methods for the measurement of colloidal concentration.

Finally, I will look at unmet challenges in the characterisation of nanoparticles and discuss the benefits of a multimodal approach to them.

5:40pm RA+AS+BI-WeA11 Multiple Technique Analysis of Perovskite Materials used in Battery and Fuel Cell Components, Robin Simpson, P. Mack, T.S. Nunnery, Thermo Fisher Scientific, UK

Due to the worlds ever increasing energy needs, renewable sources, higher efficiency and energy storage have become important research areas. Therefore, full analysis of the materials used in such applications can add to our understanding of these emerging technologies. In many cases this will mean using several techniques on a single sample.

The chemical composition of the materials found in batteries or fuel cells play a huge part in the desired properties. An example of this is in the inclusion of Sr^{2+} in the A sites of lanthanum manganite. This increases the electronic conductivity of cathode material via the addition of electronic holes to the perovskite structure. XPS allows us to quantify the chemistry of the material and use that data to further improve its properties.

Chemical analysis of the surface of the material by XPS also allows us to identify diffusion or segregation effects that can occur once a battery material has been cycled. Once a build-up of surface material on an electrode becomes too thick ions cannot pass between them, preventing charging of a cell. Using XPS with other techniques like ISS allows us to characterise the surface material (\sim top 10 nm) and the surface monolayer.

Here we discuss a LaSrFeCoO perovskite sample typically found in fuel cell and battery cell electrode materials. XPS is used to quantify the composition of the material and identify the La chemical bonding state to find the sample contains La_2O_3 bonding. ISS is also utilised to show no significant Fe and Co at the top surface of the sample. Comparing this to the XPS data taken from the top 10 nm of the shows signs of Fe and Co depletion at the surface.

The perovskite materials are also found in solar cell components. These materials are often used due to their high efficiencies but also because the material band gap is tuneable therefore allowing us to optimise the material composition. Using a technique like REELS combined with XPS can enable us to measure the band gap of the material to reveal the efficiency as well as identify the composition. In this case the band gap of the sample was calculated at 6.3 eV using REELS.

We will also be discussing the use of coincident XPS/Raman to investigate the bulk and surface characteristics of the LaSrFeCoO sample without exposing it to atmosphere between analysis.

6:00pm RA+AS+BI-WeA12 Mapping Local Physical Properties by Combining ToF-SIMS Analysis with Advanced Scanning Probe Microscopy, Maiglid Andreina Moreno Villavicencio, N. Chevalier, J.-P. Barnes, CEA-LETI, France; P. Kermagoret, F. Lorut, ST Microelectronics, France; B. Gautier, Université de Lyon, France

The continuous miniaturization and complexity of micro-devices have pushed existing characterization techniques to their limits. The correlation of techniques has emerged to overcome this issue and provide precise and accurate characterization. We have focused our research on combining and studying the applications of two specific techniques: time-of-flight secondary ion mass spectrometry (ToF-SIMS) and atomic force microscopy (AFM). The ToF-SIMS is a high-performance technique to chemically analyze a sample in 3-dimensions with a lateral resolution of 100 nm. On the other hand, the AFM is a high-resolution technique to obtain maps of the topography and local physical properties with a lateral resolution of 10 nm.

A ToF-SIMS / AFM methodology that combine the topographical information with the chemical composition has been established [1]. It was used to achieve a topography-corrected 3D ToF-SIMS data set and maps of local sputter rate where the effect of roughness and vertical interfaces are seen. However, the correlation of these characterization techniques is not limited to these applications. Indeed, by using advanced operation modes of the AFM, maps of diverse physical properties of the sample can be obtained at the same time as the topography.

We have explored the combination of ToF-SIMS analysis with three AFM advanced modes: piezoresponse force microscopy (PFM), scanning capacitance microscopy (SCM) and scanning spreading resistance microscopy (SSRM). These operation modes respectively allow to map ferroelectric domains, to locally measure capacitance variations and to image the sample surface resistivity.

The combined ToF-SIMS / AFM methodology was applied ex-situ per individual AFM mode on diverse samples for applications focused on micro-electronics. We will present here some promising results highlighting the strength and the perspectives of the expansion of this combination to other applications.

[1] M.A. Moreno et al, J. Vac. Sci. Technol. B 36 (2018) 03F122.

Thin Films Division

Room A124-125 - Session TF+AS+EL+PS+RA-ThA

Characterization of Thin Film Processes and Properties

Moderators: Richard Vanfleet, Brigham Young University, Virginia Wheeler, U.S. Naval Research Laboratory

2:20pm **TF+AS+EL+PS+RA-ThA1 Phase Separation in III-V Semiconductor Thin Films, Mark Twigg, N.A. Mahadiq, N.A. Kotulak, S. Tomasulo, M.K. Yakes, U.S. Naval Research Laboratory**

INVITED

Phase separation in III-V semiconductor alloys remains a problem that limits the performance of electronic materials. As the first stage in a comprehensive program addressing this issue, we have begun investigating an alloy system in which only the group III elements differ: InGaAs. Lattice-matched InGaAs alloy films were deposited at three temperatures (400, 450, and 500C) by molecular beam epitaxy on a (001) InP substrate.

According to kinetic instability theory, the critical temperature for spinodal phase separation in InGaAs is 814C, a temperature well above the growth temperatures used in this study [1,2]. Dark-field (DF) cross-sectional transmission electron microscopy (XTEM), using the composition sensitive $g=002$ reflection, was used to determine the amplitude of composition modulations averaged over the thickness of the XTEM sample. The amplitude of composition modulation was found to decrease with increasing growth temperature, yielding values of 0.6, 0.4, and 0.3 atomic percent for the growth temperatures 400, 450, and 500C, respectively, a trend in accord with kinetic instability theory. X-ray reflectivity and 2-dimensional small angle x-ray measurements also indicate that the 400C growth shows significantly greater phase separation than the 450 and 500C growths. Atom probe tomography indicates that the amplitude of composition modulation for the 400C growth is approximately 1 atomic percent, a value that compares favorably with the 0.6 atomic percent measured by DF XTEM.

The range of wavelengths for lateral composition modulation is found to extend from approximately 3 to 30 nm. According to the literature, such wavelengths have been found to depend on growth temperature for a number of III-V semiconductor alloys, in agreement with predictions based on surface diffusion. Measurements of the composition modulation wavelength as a function of temperature have been performed by analyzing DF XTEM images recorded using the $g=220$ diffraction vector, from XTEM samples with the glue line along the rapidly-diffusing [110] direction. Fast Fourier Transform (FFT) power spectra recorded from each image allowed the dominant composition modulation wavelengths to be determined. Analyzing these wavelengths as a function of temperature yields the same activation energy (0.55 eV) as that found in surface diffusion measurements for In adatoms on the (001) InGaAs surface [3]; thereby confirming the role of surface diffusion in phase separation driven composition modulations.

[1] F. Glas, Phys. Rev.B, 62, 7393 (2000).

[2] I. P. Ipatova, V. G. Malyshkin, and V. A. Shchukin, J. Appl. Phys. 7198 (1993).

[3] Stevens et al., J. Appl. Phys. 121, 195302 (2017).

3:00pm **TF+AS+EL+PS+RA-ThA3 In-Situ Spectroscopic Monitoring of Methylamine-Induced Hybrid Perovskite Phase Transitions, Jonathan Meyers¹, L.Y. Serafin, J.F. Cahoon, University of North Carolina at Chapel Hill**

Lead halide perovskites have shown remarkable promise for use in thin film optoelectronic devices such as photodetectors, light-emitting diodes, and solar cells. Methods for casting thin films of perovskite have been extensively studied, and great improvements have been made in an effort to improve device efficiency and stability. A few reports have suggested some benefits to processing or post-processing techniques in a methylamine (MA) atmosphere, including healing grain boundary defects to create pinhole free films with grains on the order of tens of microns and improving crystallinity. The process can be observed spectroscopically as the MA induces a reversible phase change which bleaches the dark perovskite film. In this work, we perform the MA-treatment in a vacuum reactor while monitoring in-situ the UV-visible spectral response correlated with temperature and MA partial pressure. Clear evidence is found for the existence of a solid intermediate phase in transitioning from $\text{MAPbI}_3(s)$ to

$\text{MAPbI}_3 \cdot x\text{MA}(l)$ and back again. We construct a phase diagram and demonstrate that the critical partial pressure of the phase transition changes from 10 to 500 torr between 25 and 120 °C. By tuning the kinetics of film crystallization, compact films with domains up to 80 μm can be produced.

4:00pm **TF+AS+EL+PS+RA-ThA6 Obtaining Smooth Surfaces and Measuring Surface Roughness, Steven M. George, University of Colorado at Boulder**

INVITED

Smooth surfaces are important in many areas including friction, adhesion, optics and film growth. Smooth surfaces can be obtained from rough surfaces using chemical mechanical polishing (CMP). Rough surfaces can also be smoothed using atomic layer deposition (ALD) if the conformal ALD film thickness is comparable with the lateral length scale of the roughness. In addition, rough surfaces can be smoothed using isotropic thermal atomic layer etching (ALE) if the ALE etch depth is comparable with the width of the surface asperities. Quantifying the degree of surface roughness after CMP, ALD or ALE is challenging. Surface roughness can be obtained using atomic force microscope (AFM) or x-ray reflectivity (XRR) measurements. However, the AFM and XRR techniques do not always agree. Some of the inconsistencies are attributed to the different lateral length scales for the AFM and XRR measurements. Using both AFM and XRR to characterize surface roughness is recommended for reliable measurements. In addition, XRR measurements for surface roughness should include both specular and diffuse off-specular scattering.

4:40pm **TF+AS+EL+PS+RA-ThA8 Characterizing Ultra-thin Layer Growth and Area Selective Deposition using High Resolution Low Energy Ion Scattering (LEIS), Thomas Grehl, IONTOF GmbH, Germany; P. Br uner, IONTOF GmbH, Germany; V. Pesce, B. Pelissier, R. Gassilloud, C. Vall e, Laboratoire des Technologies de la Micro lectronique (LTM), France**

When depositing ultra thin films of only very few nm of thickness, the characterization of the early stages of film growth is crucial for the quality of the film. For example, the initial thickness distribution before layer closure, created by the nucleation mechanism, will often remain after the film is complete. To analyze these early stages of growth requires very surface sensitive analytical techniques with good detection limits.

Specifically for area selective deposition, the demand for characterization increases even further. The deposition processes get more complex, involving atomic layer or plasma etching to remove nucleation on blocked areas. This also requires means of characterization, determining the effects of etching steps on the film being created, possible contamination and the level of success of the blocking.

One technique specifically suited for this application is Low Energy Ion Scattering (LEIS). By scattering noble gas ions from the surface of the sample, the mass of the atoms in the outer atomic layer is determined non-destructively. Due to specific charge exchange processes, the peaks in the scattering spectrum correspond only to the outer atomic layer, making LEIS the most surface sensitive technique to determine the elemental composition of a surface.

In addition, information from deeper layers is available in two ways: First of all, features in the spectrum contain information about the first few nm of the sample – especially for heavier elements, the in-depth distribution can be determined non-destructively. For more complex systems or light elements, sputter depth profiling can be applied as well.

In this presentation, we will illustrate the main features of LEIS on ALD films. The main part will be on an area selective deposition (ASD) process for Ta_2O_5 films on TiN or Si. Here, plasma-enhanced ALD (PE-ALD) and various plasma or ALE like etching processes, all using fluorine-containing compounds, are used to develop a super-cycle scheme for ASD. We show the effect of the different etching methods and use sputter depth profiling to determine the distribution of F – a light element not accessible to non-destructive depth profiling in LEIS. An important result is the distribution of F close to the surface, in the bulk of the film, or at the interface.

Besides this, some further sample systems will be used to highlight the use of LEIS for ultra-thin film characterization.

5:00pm **TF+AS+EL+PS+RA-ThA9 Real-Time Monitoring of Aluminum Oxidation Through Wide Band Gap MgF_2 Layers for Protection of Space Mirrors, B.I. Johnson, T.G. Avval, G. Hodges, K. Membreno, D.D. Allred, Matthew Linford, Brigham Young University**

Because of its extraordinary and broad reflectivity, aluminum is the only logical candidate for advanced space mirrors that operate deep into the UV. However, aluminum oxidizes rapidly in the air, and even a small amount of oxide (as little as a nanometer) can have a noticeable,

¹ National Student Award Finalist

Thursday Afternoon, October 24, 2019

detrimental impact on its reflectivity at short wavelengths. Thin films of wide band gap materials like MgF_2 have previously been used to protect aluminum surfaces. Here we report the first real-time, spectroscopic ellipsometry (SE) study of aluminum oxidation as a function of MgF_2 over layer thickness, which ranged from 0 – 6 nm. SE data analysis was performed vis-à-vis a multilayer optical model that included a thick silicon nitride layer. The optical constants for evaporated aluminum were initially determined using a multi-sample analysis (MSA) of SE data from MgF_2 protected and bare Al surfaces. Two models were then considered for analyzing the real-time data obtained from Al/ MgF_2 stacks. The first used the optical constants of aluminum obtained in the MSA with two adjustable parameters: the thicknesses of the aluminum and aluminum oxide layers. The thicknesses obtained from this model showed the expected trends (increasing Al_2O_3 layer thickness and decreasing Al layer thickness with time), but some of the Al_2O_3 thicknesses were unphysical (negative). Because the optical constants of very thin metals films depend strongly on their structures and deposition conditions, a second, more advanced model was employed that fit the optical constants for Al, and also the Al and Al_2O_3 thicknesses, for each data set. In particular, the Al and Al_2O_3 thicknesses and optical constants of Al were determined in an MSA for each of 50 evenly spaced analyses in each four-hour dynamic run performed. The resulting optical constants for Al were then fixed for that sample and the thicknesses of the Al and Al_2O_3 layers were determined. While the first and second models yielded similar Al and Al_2O_3 thickness vs. time trends, the film thicknesses obtained in this manner were more physically reasonable. Thicker MgF_2 layers slow the oxidation rate of aluminum. The results from this work should prove useful in protecting space mirrors prior to launch. Detailed surface/material analysis by X-ray photoelectron spectroscopy will also be shown, as well as more advanced SE modeling.

5:20pm **TF+AS+EL+PS+RA-ThA10 Visualization of Ultrafast Charge Motion in Thin Films via THz Emission Spectroscopy, Aaron Lindenberg**, Stanford University **INVITED**

We describe a method for probing ultrafast time-dependent currents in thin films and heterostructures by recording the associated emitted electromagnetic fields. This detection scheme offers direct sensitivity to the flow of charges at the atomic-scale and enables a real-time probe for investigating ultrafast charge transfer processes at molecular interfaces. Applied to transition metal dichalcogenide heterostructures having a staggered (Type-II) band alignment, we observe a burst of electromagnetic radiation at terahertz frequencies following above gap excitation. The emitted electric field transients encode information about the charge transfer within the heterostructure. The polarity of the emitted field reflects the direction of the charge transfer and the polarity is reversed as the order of the bilayer within the heterostructure is altered. We find that the charge transfer proceeds at an ultrafast rate (~ 100 fs) indicating a remarkable efficiency for the charge separation across these atomic-scale bilayers.

We will also describe initial experiments and coupled theoretical efforts probing charge separation and ultrafast photovoltaic responses in multiferroic BFO periodic domain structures. We show that charge separation occurs dominantly at the domain walls and provide a quantitative estimate of the efficiency of this process.

Bold page numbers indicate presenter

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