Wednesday Morning, September 24, 2025

Applied Surface Science
Room 209 B W - Session AS-WeM
Quantitative Surface Analysis II

Moderators: Hong Piao, FUJIFILM Electronic Materials USA., Inc., **Samantha Rosenberg**, Kairos Power

8:00am **AS-WeM-1 Using X-ray Photoelectron Spectroscopy to Determine Iron Oxidation State in Metamorphic Fe-Ti-oxides, Adirondack Mts, New York***, **Jennifer Mann**, David Valley, Kateryna Artyushkova,* Physical Electronics*; William Nachlas, John Valley,* Department of Geoscience, University of Wisconsin

This presentation explores the application of X-ray Photoelectron Spectroscopy (XPS) for analyzing geological samples, specifically a rock sample from the Adirondack Mountains, N.Y. [1] The Adirondacks are notable due to their complex history and high-temperature metamorphic mineral compositions.These rocks represent the roots of an ancient mountain belt that have been exposed by uplift and erosion. The central Adirondack Highlands were metamorphosed, 1090 to 1020 million years ago, at pressures of ~0.8 GPa (depths of ~25 km) and temperatures up to 850 °C, transforming the mineral-chemistry of many of the rocks. [2-3] The unique geochemistry provides an interesting test case for applying XPS analysis to this metamorphic transformation.

Of particular interest to geochemists is the ability to determine the Fe^{2+}/Fe^{3+} ratio in ilmenite and magnetite that can be used to infer peak-metamorphic temperatures.Traditional techniques like electron microprobe analysis have limitations in accurately differentiating these oxidation states. XPS, with its capability for detailed chemical state analysis, offers a promising complementary technique.However, Fe oxides are notoriously difficult to separate when multiple species are present, due to peak overlaps and changes in relative intensities of the satellite structure.[4] A library of Fe^{2+}/Fe^{3+} results for quantitative analysis is important for successful identification. In addition to a polished Adirondack rock sample, multiple hematite, magnetite, and ilmenite standards were measured.This library will be used to determine the oxidation states of iron within the rock's mineral phases.

The PHI *Genesis* has unique XPS capabilities in that it scans a focused (< 5 µm) X-ray beam across the sample surface.Using a combination of an optical image and PHI's unique scanning X-ray imaging capability, areas of interest on the petrographic thin section can be found quickly. The PHI scanning microprobe enables XPS analysis exclusively from ilmenite or magnetite sections of the rock. The Fe $2p_{3/2}$, Fe 3p, O 1s and valence band spectra from each of these two areas will be analyzed, by comparing relative intensities and binding energies of the peaks and satellite structures when present.

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8:15am **AS-WeM-2 Detection of Low Levels of Oxygen in Reactive Materials by X-Ray Photoelectron Spectroscopy (XPS)***, **Jeff Shallenberger**, Robert Hengstebeck,* Pennsylvania State University*; Gilbert Rayner Jr.,* Kurt J. Lesker

Accurate detection of low levels of elements such as carbon and oxygen by ion beam sputtering techniques is complicated because those elements (as well as hydrogen) are the primary constituents of the residual gas molecules present in ultrahigh vacuum systems. In this paper we determine the minimum exposure of titanium to the vacuum is only 0.1 Langmuir (1 L = 10^{-6} Torr-sec) before detectable levels of adsorbed oxygen artificially raise the measured concentration. Despite this limited analytical window oxygen detection limits of 0.3-0.4 atom% can be achieved by x-ray photoelectron spectroscopy. We apply similar approaches to aluminum nitride and titanium nitride thin films grown by atomic layer deposition techniques to show best practices for detecting low levels of carbon and oxygen. A linear relationship between exposure and oxygen adsorption at exposures <4 L was observed for all materials studied.

8:30am **AS-WeM-3 Analysis Related Artefacts in the XPS Studies of MXEnes***, **David Morgan**,* Cardiff University, UK

MXenes are a class of two-dimensional inorganic compounds consisting of atomically thin layers of transition metal carbides, nitrides, or carbonitrides. MXenes possess excellent mechanical, electronic and optical properties, and consequently their application in a diverse range of scientific areas has been explored.

Given these intriguing properties, many XPS studies have been performed, resulting in critical analysis of the spectra and the decoupling of chemical state information therein, such as that in [1]. Further studies have shown that MXEne materials age in air with the growth of a TiO_2 phase and that controlled storage can inhibit or minimise such growth to times approaching 1 year of storage [2].

Herein it is shown that XPS analysis of these materials can lead to analysis induced changes at the surface, which to the best of our knowledge has not been previously reported and discuss strategies to minimise such changes and to extract meaningful analysis from damaged spectra.

References

[1]V. Natu et al., *Matter*, 4 (2021) 1224-1251

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Acknowledgements

This work acknowledges the authors' provision of the EPSRC National Facility for Photoelectron Spectroscopy (HarwellXPS) under grant numbers EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1 and EP/Y023544/1.

8:45am **AS-WeM-4 Characterizing Oxide Phase Formation in Niobium-Based Superconducting Devices for NASA Astrophysics Missions***, **Femi Akinrinola**, Vikum Dewasurendra, Seth Woodwyk, Aidan Sheppard, Matthew Johnson, Mikel Holcomb,* West Virginia University, USA

In NASA astrophysics missions, extremely sensitive detectors are required to capture faint signals from distant astronomical sources, particularly in the far-infrared to microwave regions of the spectrum. Emerging technologies such as microwave kinetic inductance detectors (MKID) and transition-edge sensors (TES) offer exceptional temperature resolution, yet their performance can be strongly influenced by the formation of unwanted oxide phases or other chemical changes during device fabrication. To address these issues, our research focuses on characterizing niobium (Nb)-based superconducting devices to identify and analyze the oxide phases forming on their surfaces. By integrating multiple material characterization techniques, we aim to understand how these oxide layers evolve and influence device performance. We utilize X-ray absorption spectroscopy (XAS) at synchrotron light sources to probe the near-surface region of the devices at nanometer-scale depths, providing detailed insights into the chemical states and electronic structure of niobium oxides. Our XAS analysis reveals the presence of multiple niobium oxide phases, including potentially metastable forms, which may play a critical role in degrading the superconducting properties of these detectors. X-ray photoemission spectroscopy (XPS) provides complementary support for these results. These findings help us correlate fabrication processes with the evolution of surface oxides, contributing to NASA's broader goal of optimizing detector performance for future space-based missions. This research is ongoing, and current efforts are focused on refining spectral fitting models, generating high-quality reference spectra for less stable Nb oxide phases, and enhancing the accuracy of phase quantification to better inform device design and fabrication protocols. We acknowledge support from NASA 80NSSC22M0173 and NSF 2417349.

9:00am **AS-WeM-5 Challenges in Next Generation Semiconductor Devices: Insights by Tof-Sims***, **Rita Tilmann**, Alexis Franquet, Paul van der Heide,* IMEC Belgium **INVITED**

The semiconductor landscape is advancing, fuelled by evolvements such as the recently enacted European Union's Chips Act, promoting sustainability, and addressing the growing demand for higher performance in electrical devices. As the electrical industry increasingly prioritizes device miniaturization, there is a concurrent necessity for improved resolution metrology.

There is a marked expansion in the variety of applied materials that extend beyond traditional silicon leading to the integration of nanoscaled materials such as carbon nanotubes (CNTs) and two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs), as well as organic and DNA-based electronics. This wide diversity at the nanoscale underscores the urgent need for advanced metrology techniques tailored to semiconductor device design.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has emerged as a leading solution for addressing these metrology requirements. It offers the capability to analyze the composition and distribution of organic and inorganic materials at the nanoscale with exceptional precision. However, as the demands of semiconductor technology evolve, further improvements in TOF-SIMS methodologies are essential. Innovations such as the Self-Focusing SIMS (SF-SIMS) principle [1] and alternative erosion beam options, like oxygen gas cluster ion beams (O_2 GCIB), represent promising advancements. These enhancements can significantly improve the depth resolution and lateral precision of analyses for thin layered semiconductor stacked and patterned structures.

In this contribution examples of the new generation cFET analyses with TOF-SIMS including the beforementioned O_2 GCIB cluster in comparison to monoatomic O_2 and Cs beams is presented, finding the best compromise for increased depth resolution and sensitivity. In addition, the SF-SIMS principle is applied to enable quantification of Ge and dopants in SiGe layers.

As the industry moves forward, the focus on improving TOF-SIMS and related technologies will be vital enabling researchers and manufacturers to better characterize the increasingly complex nanoscaled materials and structures integral to next-generation semiconductor devices.

[1] A. Franquet, B. Douhard, D. Melkonyan, P. Favia, T. Conard, W. Vandervorst, Applied Surface Science 365 (2016) 143–152

[2] S. Holzer, S. Krivec, S. Kayser, J. Zakel, H. Hutter, Analytical Chemistry 89 (2017) 2377-2382

9:30am **AS-WeM-7 XPS Investigation of Argon Monoatomic and Gas Cluster Ion Beam Etching of 4H SiC**, ***Ryan Raad,*** Christian Doppler Laboratory for Sustainable Silicon Carbide Technology, Institute of Sensor and Actuator Systems, TU Wien, Austria*; Markus Sauer,* Analytical Instrumentation Center, TU Wien, Austria*; Georg Pfusterschmied,* Christian Doppler Laboratory for Sustainable Silicon Carbide Technology, Institute of Sensor and Actuator Systems, TU Wien, Austria*; Ulrich Schmid,* Institute of Sensor and Actuator Systems, TU Wien, Austria

Depth profiling is commonly used in spectroscopic analyses, but it can significantly alter the chemical stoichiometry and crystalline structure due to ion-matter interactions, such as mixing, cascade collision, amorphization, or diffusion[1,2]. In compound materials like SiC, preferential etching worsens the overall situation, which can yield misleading analyses. The gas cluster ion beam (GCIB) technique has emerged as a promising solution, notably known for its low-damage irradiation[3]. However, sputtering parameters must be carefully tuned as even with this technique, destructive effects on inorganic materials were demonstrated[4]. Therefore, understanding the surface modification of innovative semiconductors such as 4H SiC is crucial to minimizing sputtering artifacts and ensuring accurate device analysis.

We investigated the sputter-etching behavior of Argon monoatomic and GCIB on the Si-face of monocrystalline 4H SiC samples. The surfaces were analyzed with XPS after 15 minutes of in-situ sputtering with Ar^+_n GCIB, followed by a 1-minute aggressive Ar^+ etching (4 kV, 1.9 µA) to magnify the contrast. Figures 1 and 2 show that increasing the energy and size of the cluster drastically changes the surface composition. As illustrated in Figure 1, for 2.5 kV 10 nA (blue) and 5 kV 20 nA (green), the oxygen signal undergoes a significant reduction only after switching to aggressive etching. We can assume that for a transferred energy of up to 3.8 eV/atom with a cluster of 1300 atoms, both the silicon oxycarbide (SiCxOy in violet at 101 eV on the Si 2p) and the 4H-SiC remain intact, while the adventitious carbon is sputtered away. However, when the impact energy is further increased
(10 kV 30 nA), the oxide is etched within the first 5 minutes (see Fig. 1) and the Si 2p detailed spectrum (see Fig. 2) broadens towards lower binding energy (Si-Si in red at 99.4 eV on the Si 2p). This reduction in the oxidation state of the silicon may suggest preferential etching of the oxide, as evidenced by a decrease in its FWHM value from 1.74 eV to 1.23 eV.

Acknowledgements

The financial support from the Christian Doppler Research Laboratory for Sustainable Silicon Carbide Technology is gratefully acknowledged, as well as the training and access to XPS from the Electrochemical Surface and Interface Analysis Cluster of TU Wien.

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[3]: I. Yamada, J. Matsuo, *MRS Online Proceedings Library* **396,** 149 (1995)

[4]: A. J. Barlow, J. F. Portoles, P. J. Cumpson*, J. Appl. Phys.***116,** 054908(2014)

9:45am **AS-WeM-8 Low Energy Ion Scattering Analysis of GC/IrO_x /SiO_2 Catalyst Layer Structures***, Philipp Brüner, **Thomas Grehl,*** IONTOF GmbH, Germany*; Rens Kamphorst, Katherine Encalada-Flores, Ruud Kortlever, Ruud van Ommen,* Delft University of Technology, Netherlands

Although atomic layer deposition (ALD) offers a precise method for growing ultra-thin coatings with sub-nm control due to its self-limiting nature, characterizing these films remains challenging for surface analytical techniques. This difficulty is particularly pronounced for ultra-thin films consisting of only a few atomic layers or even sub-monolayers, as most analytical methods lack sufficient surface sensitivity and often yield averaged information that includes both the deposited film and the underlying substrate.

In this study, we apply low-energy ion scattering (LEIS) to analyze SiO_2 films grown via ALD on an electrodeposited IrOx catalyst layer on glassy carbon (GC). LEIS records the energy spectrum of noble gas ions (He, Ne, Ar) scattered from the sample surface, where the elemental peaks correspond to the composition of the outermost atomic layer, enabling quantitative analysis [1]. This extreme surface sensitivity of just a single atomic layer combined with sensitive and quantitative elemental composition analysis is unique to LEIS, making it particularly valuable for investigating ultra-thin films. Additionally, signals from sub-surface scattering provide insights into sample composition and layer thickness up to 10 nm, depending on the material.

By leveraging both top atomic layer sensitivity and thickness information, we demonstrate how to quantify the surface coverage of SiO_2 films, detect surface impurities with high sensitivity, and assess the growth mode of the films. While ALD is often expected to produce films in a well-controlled layer-by-layer fashion [2], our results on these specific samples indicate varying degrees of island growth, where some regions of the substrate develop multilayer films early in the deposition process, while others remain largely uncoated. SiO_2 films grown using different ALD processes are presented, showing the differences in film formation depending on the growth conditions clearly picked up by LEIS.

[1] "Low-Energy Ion Scattering" in Characterization of Materials - Second Edition ISBN 978-1-118-11074-4 - John Wiley & Sons.
[2] J. R. Van Ommen, A. Goulas, and R. L. Puurunen, "Atomic Layer Deposition," in Kirk-Othmer Encyclopedia of Chemical Technology, 1st ed., Kirk-Othmer, Ed., Wiley, 2021, pp. 1–42. https://doi.org/10.1002/0471238961.koe00059

11:00am **AS-WeM-13 In situ and quasi-in situ characterization techniques for atomic-scale process development in device fabrication: focus on Area Selective Deposition process***, **Christophe Vallée,*** University at Albany-SUNY*; Marceline Bonvalot,* Grenoble Alpes University, France*; Remy Gassilloud,* CEA-Leti, France*; Cedric Mannequin,* University of Nantes, France*; David Muñoz-Rojas,* Grenoble Alpes University, France **INVITED**

In the recent years, innovative processes have enabled scaling nodes through the integration of new materials and new architectures at the nm scale. 3D NAND based on multi-layering needs highly selective process. The enhancement of DRAM from 1Y-1Z needs high aspect ratio processes. Sub 3nm logic development will need precision patterning process. Most of these requirements cannot be met without the use of atomically controlled processes. Hence, the latest generation of transistors need to integrate dozens of atomic layer deposition (ALD) steps and a few atomic layer etching (ALE) steps. The next generations will certainly include selective deposition steps with the use of an area selective deposition (ASD) process. An ASD process is designed to selectively deposit material only on a surface named growth area, with no deposition on a targeted surface named non growth area. This process can be carried out using chemical deposition processes, the most popular of which is ALD. It can also be coupled with an ALE etching process to form an ASD process by super-cycling od deposition and etch. Inhibitors can also be used to block the growth on the non-growth area. The processes described below require a perfect understanding and control of the interactions between molecules/radicals and surface chemical groups. This highlights the need for in situ and quasi-in situ techniques. In this presentation, we will address the methods most widely used to date. Then we'll look ahead to HVM applications, discussing current needs in metrology, not only for process monitoring, understanding and control, but also for better measurement of process-induced defects and Yields.

11:30am **AS-WeM-15 Combining ISS, XPS and ion sputtering to discriminate Si-contamination from Si present in the stack of reticles for extreme ultraviolet (EUV) lithography***, **Véronique de Rooij-Lohmann**, Shriparna Mukherjee, Kleopatra Papamichou,* TNO, the Netherlands Organisation for Applied Scientific Research, Netherlands

EUV lithography scanners are extremely complex machines. The heart of the machine is formed by the optical system, which consists of a series of mirrors and reticle. To avoid loss of throughput and imaging performance, these need to remain free of contamination. In spite of great effort though, contamination is hard to avoid completely, as a result of the aggressive environment in combination with the plethora of components in the EUV lithography system.

Si – being ubiquitous in the semiconductor industry – is an element of particular interest to EUV-related optics Life-time research. XPS analysis of Si-contamination on optical samples (e.g. reticles and mirrors) is hindered though by the presence of Si in the sample stack. Because reference data from known clean samples is usually unavailable, the discrimination between Si as contaminant and Si as sample constituent relies on assumptions. Therefore, to advance this aspect of reticle metrology, we intentionally contaminated samples with Si, then investigated and compared several approaches to distinguish between Si on the surface and Si in the stack.

The metrology includes methods based on depth-resolved information from AR-XPS and HAXPES, Ion Scattering Spectroscopy as extremely surface-selective analysis method, and removal of the Si-contamination via mild etching with monatomic He^+, monatomic Ar^+, and Ar_{1000}^+ cluster ions. The suitability of these methods are first tested on model Ru- and absorber samples without Si in the stack. The most promising approaches are then applied to EUV reticles.

This project is supported by the Chips Joint Undertaking (under grant agreement No 101096772) and its members, including the top-up funding by The Netherlands.

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11:45am **AS-WeM-16 Using X-Ray Induced Auger Electron Spectroscopy Transitions to Explore the Surface Reactivity of Semi-Conductors***, Kirène Gaffar, Anna Gagliardi, Antonin Frappreau, Arnaud Etcheberry, Muriel Bouttemy, **Solène Béchu**,* CNRS, ILV, France

With the exception of the modified Auger parameter, X-ray induced Auger electron (X-AES) transitions remain underexploited to date. Indeed, they can provide a powerful insight for the chemistry evolution of semi-conductors (oxidation degree, chemical environment, atomic composition), as the classic photopeaks used in XPS. However, a direct interpretation (spectral signature, energy position) is not always straightforward or evident, requiring further data processing using specific decomposition procedures to take into account the complexity inherent in the shapes of these peaks.

The present work explores the decomposition of X-AES transitions by using two different methods of decomposition, the non-linear least square (NLLS) [1] and the linear least square (LLS) [2] methods. These are combined with principal component analysis and vectorial method [3]. The NLLS method requires multiple peaks to simulate the decomposition, which increases the potential for human error. However, minor adjustments can be performed with respect to position or FWHM values. In contrast, the LLS method employs a single envelope per chemical environment, which limits the decomposition error but excludes any small adjustments.

Following the implementation of different decomposition processes on Auger lines, three different applications of X-AES lines are presented. The first application involves the quantification of nitrogen in GaN material by XPS (performed with an Al Kα source), where the N 1s signal is overlaid with the Ga $L_2M_{4,5}M_{4,5}$ Auger line.[4] The second application is related to the kinetic aspect of the oxides formation of a solar absorber ($Cu(In,Ga)Se_2$ -CIGS- material). In order to explore similar depth probed (with an Al Kα source), Auger transitions and XPS photopeaks with similar escape depths are coupled for each CIGS element. This coupling method is also employed to study the surface reactivity of CdTe materials when exposed to air, with a specific input on the decomposition of Cd $M_{4,5}N_{4,5}N_{4,5}$ X-Auger lines.

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