Applied Surface Science
Room 117 - Session AS-WeM

Quantitative Surface Analysis

Moderators: David Morgan, Cardiff University, **Samantha Rosenberg**, Lockheed Martin

8:00am **AS-WeM-1 Analyzing the Extrinsic Inelastic Background of HAXPES Spectra Accounting for X-Ray Extinction in an Iron Oxide Finite Thickness Film**, *Dulce-Maria Guzman-Bucio, O. Cortazar-Martinez,* CINVESTAV-Unidad Queretaro, Mexico; *D. Cabrera-German,* Universidad de Sonora, Mexico; *J. Torres-Ochoa,* Universidad Politecnica de Juventino Rosas, Mexico; *A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico; *O. Ceballos-Sanchez,* Universidad de Guadalajara, Mexico; *W. Limestall, Z. Lee, J. Terry, M. Warren,* Illinois Institute of Technology; *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

The extrinsic inelastic part of the background is part of all photoemission spectra. Its identification and modeling, as well as other background contributions, play a crucial role in assessing the peak signal used in the quantification of chemical composition. However, existing methods cannot directly apply to finite-thickness films because they only apply to semi-infinite-homogeneous samples [1]. Moreover, they are not appropriate for spectra obtained with Hard X-ray Photoemission Spectroscopy (HAXPES), where the mean free path of the photoelectrons may be comparable to the absorption length of the photons at certain incident angles.In this study, we model the extrinsic inelastic background for photoemission spectra for a finite-thickness Fe_2O_3 film for which a grazing X-ray incident angle was employed. We analyzed Fe $2s$, $2p$, $3s$, and $3p$ photoemission spectra acquired with synchrotron light at eight photon energies around the Fe $1s$ threshold at Beamline 10-ID-B at the Argonne National Laboratory. Our calculations assume a straight-line inelastic scattering path and account for the decay of the X-rays as they travel through the sample [2]. It was assumed that the inelastic electron cross section (λK) for iron oxide does not change drastically for electron primary energies higher than 2 keV, and one acquired at this primary electron energy was employed [3]. The comparison with the experimental data and information about sample processing shows great agreement.

This presentation summarizes the requirements and challenges involved in correctly analyzing the extrinsic inelastic background of HAXPES data. This includes using appropriate inelastic mean-free paths and effective attenuation lengths. Obtaining REELS data along with photoemission data, and calculating inelastic electron cross sections for primary excitation energies in the hard X-ray regime is essential.

[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. https://doi.org/10.1103/PhysRevB.25.4452.

[2] A. Herrera-Gomez, The photoemission background signal due to inelastic scattering in conformal thin layers -Internal Report, 2019.

[3] N. Pauly, F. Yubero, J.P. Espinós, S. Tougaard, Optical properties and electronic transitions of zinc oxide, ferric oxide, cerium oxide, and samarium oxide in the ultraviolet and extreme ultraviolet, Appl. Opt. 56 (2017) 6611–6621. https://doi.org/10.1364/AO.56.006611.

8:15am **AS-WeM-2 Non-Destructive Characterization of Multi-Layered Thin Films Using XPS, HAXPES and Structure Modeling in StrataPHI**, *N. Biderman, D. Watson, Kateryna Artyushkova,* Physical Electronics USA

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

In this talk, we will show that the *Strata*PHI software has been further developed to combine Al Kα and Cr Kα XPS and HAXPES data within a single depth profile to enhance extracted analytical information from various depths below the surface. We will explore the method of the combined technique as well as its application to multilayered thin film samples. Such added *Strata*PHI capabilities allow for scientists and engineers in metrology and research & development to analyze multi-layered thin films and ultra-thin films rapidly and non-destructively without potentially damaging ion beam sputtering that might otherwise be required to depth-profile or sputter-clean adventitious contamination off the surface.

8:30am **AS-WeM-3 The Challenge of Quantifying Photoemission Spectra Using Multiple Photon Energies**, *Thierry Conard, A. Vanleenhove,* IMEC, Belgium; *I. Hoflijk, I. Vaesen,* IMEC Belgium **INVITED**

The development of Photoemission spectroscopy in laboratories during the last decades has been focused on the use of AlKa radiation. Extensive work has been performed to tackle the issue of quantification of acquired spectra. These include aspects such as the determination of sensitivity factor, understanding spectral background, determining transmission function of spectrometers, and understanding electron transport inside materials (inelastic mean free path, ...).

The use of higher energy photons (HAXPES) has the potential to significantly increase the application field of PES due to its larger depth information making it more suitable for multilayers systems. One of the major limitations of HAXPES is the strong decrease of the photoemission cross-section at higher photon energy which, until a few years ago limited the use of HAXPES to synchrotron, where higher photon flux are achieved than in laboratory instruments. As such, the challenges to quantify HAXPES spectra do not differ significantly from lower photon energy experiment, but this was not the prime focus of synchrotron-based experiment. With the introduction of performant laboratory-HAXPES systems a few years ago, the need of better quantification for HAXPES has strongly been increasing.

In this presentation, we will start by presenting examples of the efforts made regarding the development of reliable quantification protocols, based, as for AlKa-based PES data, on the determination/analysis of sensitivity factors, background, transmission function, ...

Next to the "classical" challenges, some additional aspects need (more often) to be considered. First, energy referencing is critical for chemical state quantification. It is however more complex than with lower energy PES as it is very impractical to use contamination peak for referencing and the likelihood of vertical potential variations increases. Second, thanks to the larger photon energy, for many elements, additional photoemission peaks are available for analysis and peak-independent quantification would be interesting. For both aspects, we will present examples of applications and improvement.

Unfortunately, even if all the above-mentioned challenges would be solved, depending on the scientific question to be answered a single experiment may require the use of multiple photon energies, for instance for varying the analysed depth or improving on the chemical identification. We will discuss strategies to combine analysis with multiple photon energies to achieve the best possible understanding of the studied system. This will include consideration about results presentation for a better understanding by non-specialist.

9:00am **AS-WeM-5 Angle-Resolved XPS Depth Profiling for Extreme Ultraviolet (EUV) Lithography Optics Research – Monoatomic vs Cluster Ion Source**, *Veronique de Rooij-Lohmann, S. Mukherjee,* TNO Science and Industry, the Netherlands; *J. Counsell,* Kratos Analytical Limited, UK

In the Semicon Equipment Life-time department of TNO, X-ray photoelectron spectroscopy (XPS) analysis is utilized for characterization of optical surfaces, particularly mirrors and reticles for extreme ultraviolet (EUV) lithography. This study focuses on assessing the sensitivity of XPS depth profiling to multilayer mirrors which are similar to the EUV mirrors.

A commercial Ru-capped Mo/Si multilayer mirror was annealed in vacuum at 330 °C for 48 hours, to induce thermal degradation, i.e. intermixing and oxidation. Pre and post-annealing, traditional XPS depth profiling was conducted using a monatomic Ar ion-gun.

However, monatomic Ar+ depth profiling results in artefacts because preferential sputtering of light elements alters the stoichiometry, while ion-induced intermixing compromises layer contrast. Development of sputtering methods that reduce those artefacts is therefore of importance.

To address these challenges, we explore the potential of a Gas Cluster Ion Source (GCIS), known for minimizing the said artefacts. While GCIS is gaining traction in XPS, its applicability to EUV mirror analysis requires validation because the ion-solid interaction is material-dependent.

Moreover, given the limited thickness of the layers in an EUV-mirror compared to the XPS information depth, we also investigated the

combination of sputter depth profiling with angle-resolved (AR-)XPS to enhance the surface sensitivity. The results are shown in Figure (a) and (b). This comparative study between traditional XPS depth profiling and GCIS, along with the exploration of AR-XPS, provides insights into optimizing analysis techniques for EUV mirrors and reticles. These findings inform further development towards metrology and understanding of EUV optics degradation.

9:15am AS-WeM-6 Beyond the Surface: A Simple Algorithm for Obtaining Surface-Free Depth Distribution Information from Combined XPS and HAXPES Spectra, *Benjamen Reed,* National Physical Laboratory, UK*; J. Counsell,* Kratos Analytical Limited, UK*; A. Shard,* National Physical Laboratory, UK

There is a recurrent demand from the semiconductor, energy, and coatings industries to measure the chemical state of elements in subsurface layers. X-ray photoelectron spectroscopy (XPS) has unparalleled capabilities for chemical state measurements, but it has a limited information depth, typically around 10 nm for instruments using an Al Kα X-ray source. The traditional method for measuring subsurface chemistry is to perform a depth profile, alternating ion beam sputtering to remove surface layers and XPS measurements. Gas cluster ion beam technology has enabled damage-free sputtering of organic materials, but low sputtering rates for inorganic materials gives impractical experiment durations. Increasing the energy per atom in clusters will typically improve sputtering rates but also generates a thin altered, or damaged, layer either through chemical changes or preferential removal of elements. Some materials are particularly sensitive to ion sputtering, and so will exhibit sputtering damage regardless of parameters used during depth profiling.

To aid in the analysis of these sputter sensitive materials, we present a data processing algorithm which attempts to isolate the spectroscopic information of the undamaged subsurface material from the damaged surface material during a depth profile. The algorithm utilises the different intensity depth distributions that arise from Al Ka and Ag La X-ray generated spectra. An empirically determined scaling parameter is used to equate the surface intensity contribution from Al Ka and Ag La X-ray generated spectra, allowing a difference spectrum to be obtained that has a surface-free depth distribution, and therefore reduces (or completely removes) the intensity contribution from the sputter damaged layer. This method also works for very thin overlayers on homogenous materials, such as native oxides or adventitious carbon contamination.

9:30am AS-WeM-7 Depth Differentiated Surface Analysis by a Combination of XPS, HAXPES and Ion Scattering Spectroscopy, *Paul Mack,* Thermo Fisher Scientific, UK

Complementary multi-technique surface analysis has been available on XPS systems for many years.It is only recently, however, with the advent of more user-friendly software interfaces that these complex experiments have become routinely accessible by all users.XPS systems with easily switchable monochromated X-ray sources are now commonplace, allowing the analyst to switch between Al-Ka X-rays and some other higher energy photon source (Ag-La, for example).The use of two different X-ray energies enables some level of effective depth profiling without having to physically sputter the sample with an ion source.

XPS is known as a surface sensitive analytical technique, with Al-Ka X-rays typically enabling analysis from the top 10-15nm of the surface, depending on the material.With a Ag-La monochromated source, the sampling depth may be similar for the photoelectron signals in the higher binding energy portion of the spectrum but up to double the sampling depth for the higher kinetic energy XPS peaks.If the analyst wants to probe the very top surface, including the top monolayer, then a different analytical technique is required.Ion Scattering Spectroscopy (ISS) is even more surface sensitive than XPS and when combined with XPS and its higher energy counterpart, HAXPES, a far more comprehensive picture of the surface composition and profile can be developed.

In this work, XPS, HAXPES and ISS have been combined on a XPS system enabling non-destructive depth differentiated analysis of a variety of samples.By bringing all three techniques together the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface can be investigated.

11:00am AS-WeM-13 Femtosecond Laser Ablation (fs-LA) – A New Approach to XPS Depth Profiling, *Simon Bacon,* Thermo Fisher Scientific, UK*; S. Sweeney,* University of Glasgow, UK*; S. Hinder,* University of Surrey, UK*; A. Bushell, T. Nunney, R. White,* Thermo Fisher Scientific, UK*; M. Baker,* University of Surrey, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers by using argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed that employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (several 10s microns) and is much faster than traditional ion beam sputter depth profiling. fs-LA XPS depth profile results will be shown for selected thin films, coatings, multilayers and oxidised surfaces and the outlook for this new technique discussed.

11:15am AS-WeM-14 Top Atomic Layer Analysis of Bimetallic Nanoparticles by Low-Energy Ion Scattering (LEIS), *P. Brüner,* IONTOF GmbH, Germany*; D. Niedbalka, P. Abdala, C. Müller,* ETH Zürich, Laboratory of Energy Science and Engineering, Switzerland*; Thomas Grehl,* IONTOF GmbH, Germany

The composition of the outer atomic layer often differs significantly from subsequent layers. Since the performance of a heterogeneous catalyst heavily depends on its outer atomic layer, high surface sensitivity analytical techniques are required. Most available surface analytical techniques probe to a depth of at least a few nm. Any result will thus be an average over the first few (or many) monolayers, such that unique properties of the outer monolayer may be missed due to the diluted effect on the analysis result.

Low energy ion scattering (LEIS) is the only technique available that selectively probes the elemental composition of the outer atomic layer [1]. This is achieved by bombarding the sample surface with noble gas ions at an energy of some keV. These primary ions may scatter from surface atoms, and their characteristic energy loss is a measure for the mass of the scattering partners. Evaluating the energy spectra of the backscattered primary ions results in the quantitative elemental composition of the outer monolayer, since neutralization effectively suppresses the signal from scattering events below the outer surface.

Since LEIS is not sensitive to surface charging and topography, it is routinely applied to study (even supported and dispersed) nanoparticles and their terminating atomic layer. This contribution will introduce this application including results from several sample systems. The core results are from monometallic Co and Pt as well as bimetallic CoPt nanoparticles with varying Co/Pt ratios prepared on an SiO_2 support with a total metal loading of $1.5 – 4$ wt. %. The catalysts were activated in a 10 % H_2/N_2 mixture at 800 °C for 1 h, resulting in average particle sizes ranging from $1.7 – 3$ nm.

LEIS analyses were conducted using a Qtac 100 (IONTOF GmbH) with a double toroidal electrostatic analyzer optimized for high sensitivity and mass resolution, allowing for top atomic layer analysis without significant surface damage by the probing ion beam.

3 keV He^+ ions were used for overview scans, as all elements C and heavier can be detected by He^+ analysis. Subsequent analysis with 5 keV Ne^+ ions offers improved mass resolution and sensitivity for heavy elements. For some of these samples, sample pretreatment is more challenging than usual, due to the H physisorption on Pt which must be reproducibly reduced to yield robust results.

The LEIS results relate the bulk composition of the CoPt nanoparticles to their surface composition, catalytic activity and stability. Reference samples were used to determine the precise surface coverage of Co and Pt.

[1] Cushman, C. V. et al., *Analytical Methods* **2016**, 8, 3419

11:30am AS-WeM-15 Multilayer Adhesives-Ideal Samples for Showcasing GCIB Profiling Capabilities, *Michaeleen Pacholski, B. Caruso,* Dow Chemical Company*; I. Uhl,* Dow Chemical Company, France*; A. Peera,* dow*; D. Keely, E. Glor,* Dow Chemical Company

There are many manufacturing methods that can produce multilayer coatings, but for pressure sensitive adhesives there has been growing use of curtain coaters that can create a multilayer coating in a single step.This allows manufacturers to balance the performance and cost of each layer of the coating to the application.Most of these adhesives are around 25 µm thick, meaning accessing buried layers, which cannot be delaminated, has involved laborious sample preparation prior to the application of GCIB profiling.With the application of this multilayer coating technology new questions are being asked of the analytical group that include:Do the adhesive layers mix?Do surfactants and tackifiers migrate between the layers?If the adhesive fails cohesively, in which layer does it fail?In this presentation the curtain coating method and measurements of importance in the liquid state will be discussed, as well as GCIB approaches to answer the questions above.

11:45am AS-WeM-16 Similarities between Silicon and Aluminum with Suboxides Formation Using XPS Spectra, *Orlando Cortazar-Martinez, D. Guzman Bucio, J. Torres Ochoa, C. Gómez Muñoz, J. Raboño Borbolla, A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

Aluminum, recognized as a reactive metal, rapidly reacts with oxygen to form a dense protective layer of aluminum oxide. Its valence band contains three electrons, which can be shared to form Al^{1+}, and Al^{2+}, and Al^{+3} oxidation states; the stable form is the latter, there have been reports of the presence of the first two.

Initial oxidation stages of aluminum were achieved by exposing the surface to a precisely controlled ultra-pure oxygen atmosphere with varying gas dosages. The metallic and oxidized film was characterized with angle-resolved X–ray photoelectron spectroscopy; the data was analyzed with state-of-the-art techniques.Two surprising results were found: 1) the appearance of two extra peaks in the Al 2p spectra, corresponding to Al^{1+}, and Al^{2+} at the interface; and 2) a protrusion-mode growth of Al_2O_3.The first shows many similarities with silicon, which is the next element in the periodic table.The second is also surprising because, contrary to current perception, the oxide does not grow conformally in the initial oxidation stages; this contrasts with silicon because it does grow conformally from the very initial oxidation.

[1] A. Herrera-Gomez, F. Servando Aguirre-Tostado, and P. Pianetta, Formation of Si1+ in the early stages of the oxidation of the Si[001] 2 × 1 surface, Journal of Vacuum Science & Technology A 34, 020601 (2016).

[2] A. Herrera-Gomez, M. Bravo-Sanchez, F.-S. Aguirre-Tostado, M.-O. Vazquez-Lepe, The slope-background for the near-peak regimen of photoemission spectra, J. Electron Spectros. Relat. Phenomena. 189 (2013) 76–80.

12:00pm AS-WeM-17 3kV Vertical Gallium Nitride Photoconductive Semiconductor Switches, *Geoffrey Foster, A. Koehler, A. Jacobs, K. Hobart,* Naval Research Laboratory*; S. Lowery, S. Atwinmah, S. Mahmud, R. Khanna,* University of Toledo*; J. Leach,* Kyma Technologies*; M. Mastro,* Naval Research Laboratory

We made a 3 kV vertical GaN photoconductive semiconductor switch that has 7 orders of magnitude on/off current. Vertical PCSSs carry the potential to outperform conventional unipolar semiconductor power devices. PCSSs become conductive after the absorption of light. Wide bandgap PCSSs, are desirable due to high critical electric field strength, high electron saturation velocity, and to provide high power ultrafast devices. Lateral GaN PCSSs have been demonstrated with a fast turn on time and a high amount of on-current. Vertical GaN PCSS have been shown to operate with below bandgap excitations. A device operating with band gap excitation would be preferred for high-powered switching, as it allows faster response time and faster switching speeds. Conventional unipolar power semiconductor devices are limited by the thickness of the drift layer, needed for voltage hold-off, but adds resistance to the conduction path. A PCSS can have a semi-insulating layer in lieu of a drift layer. The conductivity of the semi-insulating layer can be optically modulated, allowing for free-carrier injection. Fast switching speeds can be obtained by optical modulation, which optically isolates the sensitive gate driver control circuitry from the high-power switch and associated electronic noise.

One hundred micrometers of GaN was grown on an N+ GaN substrate by HVPE, with a carbon doping concentration of 1×10^{18} cm^{-3} to produce vertical PCSS diodes. Electrodes of Ti/Al/Ni/Au were formed into a 615 um diameter circular patterns by lift-off on the top surface. Within the circles, a constant area of optically exposed GaN was left without metal. Square areas with sizes varying in size from 20 to 200 microns per side. Different devices were used to investigate the effects of collection area size outside of the metal contact area. Blanket Ti/Au was deposited on the backside of the wafer. I-V measurements were then performed by using a 3W, 365 nm, 46.24 mm^2 COTS LED. Electrical measurements were acquired at an optical power density of 0.102 W/cm^2. Two different resistance values were found, 1.37 Ω-cm^2 if the device was optically exposed and 1.42 Ω-cm^2 if the device was not. An additional 100 µm perimeter of a collection area outside the device accounts for the resistance variation. Devices exhibited a maximum current density of 3.63 A/cm^2 at 5 V. In the off state, devices were measured to have a current of 459 nA/cm^2 at 3 kV. Photoionization spectroscopy under monochromatic light shows a photoresponse excitation at the band gap and a carbon related excitation at 3.1 eV incident photon energy, with an on/off current of 7 and 3 orders of magnitude respectively under 5V forward bias.

Author Index

Bold page numbers indicate presenter