Applied Surface Science
Room Central Hall - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP-1 Advances in the Chemical Composition Quantification of Surface and Volume Using HAXPES Data, *Dulce-Maria Guzman-Bucio,* CINVESTAV-Unidad Queretaro, Mexico*; J. Huerta-Ruelas,* CICATA Queretaro, Mexico*; 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, M. Warren, J. Terry,* Illinois Institute of Technology*; A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

In recent decades, HAXPES has gained scientific and technological relevance.This method offers several advantages, including the capability to analyze both the surface and bulk of materials. It allows for the analysis of buried layers without requiring the removal of top surface layers by ion sputtering, thereby eliminating sample damage. Additionally, the interference with Auger signals decreases. However, there are significant challenges for quantitatively interpreting the data.

As with XPS, assessing chemical composition with HAXPES requires differential photoelectric cross-sections. For HAXPES, it is essential to consider the increasing relevance of non-dipole terms.

This study presents a summary of the requirements and challenges associated with employing HAXPES data for chemical composition analysis of iron oxide samples. Additionally, we provide insights into the application of a MultiLayer-Method to analyze multilayered films using photoemission data from a partially oxidized iron film as the X-ray crossed the iron K edge. These experiments were carried out at Beamline 10-ID-B at the Argonne National Laboratory.

AS-ThP-2 Basic Aspects of the Asymmetry of Lineshapes in Photoemission Spectra Caused by a Cascade of Excitations of Fermi-Level Electrons, *A. Dutoi,* University of the Pacific*; **Alberto Herrera-Gomez***, Cinvestav, Mexico*; D. Guzman-Bucio,* CINVESTAV-Unidad Queretaro, Mexico

The effect of cascade excitations of Fermi-level electrons on the lineshape of photoemission spectra was treated by Doniach and Sunjic (DS) in 1970.[1] Their derived lineshape has many issues such as its lack of integrability and failure to closely reproduce experimental data.[2] We analyze this problem using a formalism rooted only in the basic quantum mechanics of resonances with a minimalist diagrammatic veneer to categorize the many-body of processes (Tougaard losses, plasmons/hole-shielding, multiplet structure, and perhaps the Shirley background). The accounting for these processes can be done with varying levels of rigor, from simple consideration of energy scales, oscillator strengths, and couplings, through to *ab initio* calculations of matrix elements. A density-matrix formulation in the many-body space can be applied to remove spurious interferences of states that have ill-defined/incoherent relative phases (differ from shot to shot, due to pulse noise, sample inhomogeneities, temperature, *etc*.). In our work, we will apply the simplest level of semi-quantitative analysis to propose possible alternatives to the problematic DS lineshape. For example, an incoherent superposition of exponential decay in time yields a lineshape that is asymmetric but integrable.

[1] S. Doniach and M. Šunjic, "Many-electron singularity in X-ray photoemission and X-ray line spectra from metals," Journal of Physics C: Solid State Physics **3**, 285–291 (1970).

[2] A. Herrera-Gomez, D.M. Guzman-Bucio, A.J. Carmona-Carmona, O. Cortazar-Martinez, M. Mayorga-Garay, D. Cabrera-German, C.A. Ospina-Ocampo, B.V. Crist, and J. Raboño-Borbolla, "Double Lorentzian lineshape for asymmetric peaks in photoelectron spectroscopy," Journal of Vacuum Science & Technology A **41**(4), (2023).

[3] A. Herrera-Gomez, D. Cabrera-German, A. D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, and L. Gomez-Muñoz, "Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge," Surface and Interface Analysis **50**, 246–252 (2018).

AS-ThP-3 XPS Study of the Initial Oxidation of Iron for Ultrathin and Thick Films, *Orlando Cortazar-Martinez, J. Torres Ochoa, J. Fabian-Jacobi, J. Raboño Borbolla, A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

We studied the initial stages of oxidation of ultrathin and thick iron films on silicon. Clean films were exposed to a controlled ultra-pure oxygen atmosphere with varying gas dosages at room temperature. The characterization was done with angle-resolved XPS [1]; the data was analyzed using robust analysis techniques including the block approach [2] and simultaneous fitting, as well as background modeling with the active approach, Shirley-Vegh-Salvi-Castle (SVSC), and the Two-Parameter Tougaard background [3].

While thick films oxidize in a layer-by-layer fashion, thin films exhibit oxidation by clusters or islands. The multilayer method (MLM) was employed to quantify the ultrathin films' chemical composition and structure. In both cases, Fe_2O_3 is the oxide composition.

[1] A. Herrera-Gomez, O. Cortazar-Martínez, J.F. Fabian-Jocobi, A. Carmona-Carmona, J.G. Raboño-Borbolla, M. Bravo-Sanchez, J.A. Huerta-Ruelas, A self-consistent multiple-peak structure of the photoemission spectra of metallic Fe 2p as a function of film thickness, Surface and Interface Analysis 52 (2020) 591–599. https://doi.org/10.1002/sia.6796.

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

[3] S. Tougaard, Universality classes of inelastic electron scattering cross sections, Surf. Interface Anal. 25 (1997) 137. https://doi.org/10.1002/(SICI)1096-9918(199703)25:3<137::AID-SIA230>3.0.CO;2-L.

AS-ThP-4 Rapid Assessment of Detector Linearity and Deadtime Correction for XPS Instruments, *Benjamen Reed, A. Shard,* National Physical Laboratory, UK

Confidence in the intensity scale of a photoelectron spectrometer is vital for quantitative analysis of photoelectron spectra. This is because the integrated area under a core level peak is proportional to the atomic fraction of that element in the sample. Sample dependent factors aside, the XPS analyst must calibrate for the intensity response (or transmission function) of their analyser, which is largely a result of electrostatic lens column and is unique for each instrument. However, even before a spectrum is acquired, there must be confidence that the measured count rate of the analyser's detection system is correct. For example, at high count rates, the detector may exhibit a non-linear response that significantly effects the measured count rates, and therefore the peak intensities from which atomic fractions are calculated. At even higher count rates, detector saturation may occur. So, although it is tempting to conduct XPS measurements with increased count rates (e.g. by increasing X-ray emission with high throughput electrostatic lens modes and collimation settings) with the intent to improve signal-to-noise and reduce experiment times, this approach is stymied by the limits of the detection system itself.

Recently an interlaboratory study on XPS intensity calibration was organised by the National Physical Laboratory (NPL) under the auspices of the Versailles Project on Advanced Materials and Standards (VAMAS). In the interlaboratory study, a number of datasets on sputter cleaned gold were submitted that exhibited evidence of detector non-linearities. It appears then, that awareness of this limitation of photoelectron detectors may not be universally known throughout the XPS users' community. Therefore, we shall briefly introduce these concepts and then present a straightforward method for rapidly assessing the linearity and deadtime correction for photoelectron spectrometer detectors which is based on the spectrum ratio method from Annex A of ISO 21270 ("Surface chemical analysis — X-ray photoelectron and Auger electron spectrometers — Linearity of intensity scale").

AS-ThP-5 ASSD Student Award Finalist Talk: Dry and Wet Etching of Single-Crystal AlN, *Hsiao-Hsuan Wan[1], C. Chiang, J. Li,* University of Florida*; N. Al-Mamun, A. Haque,* Penn State University*; F. Ren, S. Pearton,* University of Florida

The dry etching of high crystal quality c-plane AlN grown by Metal Organic Chemical Vapor Deposition was examined as a function of source and chuck power in Inductively Coupled Plasmas of Cl_2/Ar or $Cl_2/Ar/CHF_3$. Maximum etch rates of ~1500 Å•min^{-1} were obtained at high powers, with selectivity over SiO_2 up to 3. The as-etched surfaces in $Cl_2/Ar/CHF_3$ have F-related residues, which can be removed in NH_4OH solutions. The Al-polar basal plane was found to etch slowly in either KOH or H_3PO_4 liquid formulations with extensive formation of hexagonal etch pits related to dislocations. The activation energies for KOH or H_3PO_4 -based wet etching rates within these pits were 124 and 183 kJ/mol, respectively, which are indicative of reaction-limited etching.

AS-ThP-7 Probing the Adhesive / Substrate Interface Using Back Side Sims Profiling Facilitated by Releasable Thin Metal Films, *Paul Vlasak, S. Altum, T. Fielitz, J. Beebe,* Dow Chemical Company

Depth profiling using secondary ion mass spectrometry (SIMS) or other surface sensitive methods is an attractive strategy for studying cured adhesive or sealant compositions near their interfaces with substrate materials to take advantage of the extraordinary depth resolution of these methods. A classic problem with this approach is that a poor performing sample may exhibit adhesive failure, so that the interface of interest can be easily exposed and ideally presented to the analyzer, while the exemplary sample exhibits cohesive failure, and the interface of interest remains hopelessly buried beneath an irregular layer of adhesive. Here we present one approach to facilitate back side profiling from the substrate side, allowing analysis of the interface of interest without requiring adhesive failure at the interface. In the demonstrated approach, a 20 nm thick layer of aluminum was deposited on a sacrificial polymer film. The adhesive of interest was cured against the aluminum surface under varying environmental cure conditions. The polymer film was then peeled away, leaving the thin aluminum layer intact on the adhesive. SIMS depth profiles through the aluminum into the adhesive allowed a direct comparison of near surface chemical composition, revealing different distributions of formulation components depending on cure conditions.

AS-ThP-8 Probing the Effects of Surface Chemistry on Quality Factor and Coherence Times of Superconducting Radio Frequency Cavities and Qubits, *Adam Clairmont, J. Lee, A. Murthy,* FermiLab

Understanding the chemistry of both surface and bulk properties is important for improving the performance of superconducting radio frequency (SRF) cavities and superconducting qubits. Utilizing state-of-the art material characterization tools, researchers can better understand the impact subtle changes in chemistry have on quality factors and coherence times of such devices. Fermilab's Material Science Laboratory co-operated by the Applied Physics and Superconducting Technology Directorate and Superconducting Quantum Materials and Systems Center houses a custom-built x-ray photoelectron spectroscopy (XPS) instrument that was designed with the characterization of SRF cavities and qubits in mind.

A monochromatic silver anode accompanies the standard monochromatic aluminum anode. This allows the researcher to increase their information depth from 9-10 nm (Al) to 17-20 nm (Ag), access a greater number of core levels, and to shift Auger transitions to avoid possible peak overlaps. Using a small spot lens mode, XPS mapping can be done with <30um achievable spatial resolution. If increased spatial resolution is needed, the electron source can be used for Auger or scanning Auger microscopy with sub-micron spatial resolution. Band gaps can be analyzed with the Helium (I and II) ultraviolet source. An argon gas cluster ion beam with selectable cluster size, monatomic-3000 Ar ions per cluster, allows rapid low-damage sputtering. A high-pressure chamber can reach temperatures approaching 1073 Kelvin (K) while also introducing gasses such as nitrogen, oxygen, hydrogen, carbon dioxide, and various inert gasses up to pressures of 20 bar. As this chamber is directly attached to the system, samples can be transferred into the load lock and into the analysis chamber following heat treatments without exposure to air. Finally, a liquid helium manipulator is coupled with an e-beam heater for *in situ* characterization from less than 15K to 1073K.

This unique tool has enabled a wide variety of scientific studies that have improved our understanding of sources limiting the performance of SRF

cavities as well as superconducting qubits and I will present results from some of these efforts.

AS-ThP-9 Electronic Structure in a Transition Metal Dipnictide TaAs$_2$, *S. Regmi,* Idaho National Laboratory*; Arun Kumar Kumay, M. Neupane,* University of Central florida

The family of transition-metal dipnictides (TMDs) has been of theoretical and experimental interest because this family hosts topological states and extremely large magnetoresistance (MR). Recently, TaAs$_2$, a member of this family, has been predicted to support a topological crystalline insulating state. Here, by using high-resolution angle-resolved photoemission spectroscopy (ARPES), we reveal both closed and open pockets in the metallic Fermi surface and linearly dispersive bands on the (-201) surface, along with the presence of extreme MR observed from magneto-transport measurements. A comparison of the ARPES results with first-principles computations shows that the linearly dispersive bands on the measured surface of TaAs$_2$ are trivial bulk bands. The absence of symmetry-protected surface state on the (-201) surface indicates its topologically dark nature. The presence of open Fermi surface features suggests that the open-orbit fermiology could contribute to the extremely large MR of TaAs$_2$.

AS-ThP-11 Analysis of High-k Metal Stacks by Hard X-Ray Photoelectron Spectroscopy Under Bias, *Anja Vanleenhove, T. Conard,* IMEC Belgium*; D. Desta, H. Boyen,* Hasselt University, Belgium

While the replacement of SiO2 by high-k materials started in the early 2000s, the need for a deep knowledge of band-energies in complex high-k stacks is a hot topic in research and development in the advanced CMOS industry.

Although XPS is most commonly used as a technique to study the chemical composition of the top surface and thin layers plus interfaces in the top of the stack, *Kumar et al.* have demonstrated how the technique could be used to examine band-energies in high-k metal stacks with the established XPS using Al Kα radiation. For XPS using Al Kα, the analysis depth is limited to the top 5-10 nm. With the recently developed laboratory based hard X-ray photoelectron spectroscopes (HAXPES) the path is opened to the analysis of thicker stacks and deeper buried interfaces (20-50 nm).

In this work, we will demonstrate the use of HAXPES under bias to examine relevant high-k metal stacks and illustrate that, as is the case for all other analysis techniques, this technique has its own limitations as well.

The examined samples and measurement set-up are modelled to enable an effective biasing across the stack while executing the HAXPES measurement. The samples consist of Si/SiO2 substrates topped with high-k materials Al2O3 and HfO2 which are covered with TiN. The sample matrix is designed to study different stack orders of the high-k materials as well as different high-k layer thicknesses. HAXPES measurements are executed on the *HAXPES Lab* of Scienta Omicron, a tool which combines a high flux monochromated Ga Kα X-ray source of 9252.1 eV with an Al Kα X-ray source of 1486.6 eV.

Reference: P. Kumar *et al*., "Development of X-ray Photoelectron Spectroscopy under bias and its application to determine band-energies and dipoles in the HKMG stack," *2018 IEEE International Electron Devices Meeting (IEDM)*, San Francisco, CA, USA, 2018, pp. 17.6.1-17.6.4, doi: 10.1109/IEDM.2018.8614554.

AS-ThP-13 Update on Using Different Instruments on the Same Sample and Getting Similar Results, *Lyndi Strange, D. Baer, M. Engelhard, V. Shutthanandan,* Pacific Northwest National Lab*; A. Shard,* National Physical Laboratory, U.K.

Literature analyses indicate growing use of XPS in multiple disciplines and increasing observations of faulty analysis. To ensure reliable results, detailed attention is required to acquisition and analysis. Our laboratory has instruments from three vendors, and it may be necessary to collect data from the available instrument. Users often export data for analysis using alternative software. It is useful to know the consistency of data collected on "identical" samples on different systems and analyzed using "native" (or blind) data export to other software packages. This paper describes what we thought was a "simple" test of data collection on three different systems and analysis using the native software for each system and analysis when naively exported to a non-native software package.Copper foil was the test specimen from which survey and high-resolution spectra were collected using Kratos Axis DLD Ultra, Thermo-Fischer NEXSA, and Phi Quantera spectrometers. Using both survey and narrow window data, the analyses included: i) comparison of Cu 3p and Cu 2p peak ratios, ii) Cu 3p and Cu 2p atom ratios using native software and iii) when exported to CasaXPS. We also compared the wide scan spectra shapes to the ideal Cu

spectra provided by the National Physical Laboratory to obtain an approximate instrument response function. Although simple in concept, these comparisons were found to be less than straightforward. High count rate survey spectra ratioed to the ideal spectra produced unexpected variations in the instrument response functions. These ratios made more sense when count rates were reduced by lowering the X-ray intensity or decreasing the pass energy.Cu 3p and Cu 2p peak ratios were determined using peak intensities after removal of an iterated Shirley background between 58.0 eV and 91.0 eV for Cu 3p and 920.0 eV to 970.0 eV for Cu 2p.Because of variations in the instrument geometry and transmission functions, raw peak ratios among the three spectrometers differed by > 2.However, native software analysis on each instrument produced similar amounts of Cu to roughly ± 5%. Note that sensitivity factors are more established for Cu 2p peaks than for Cu 3p peaks which may account for some variation. Naive transfer of data for analysis by non-native software was found to produce results significantly different than expected in some cases.This can be due to sensitivity factors or complications related to the instrument response function. These issues can be corrected but require care and verification or incorrect results will result.

AS-ThP-14 ToF-SIMS Characterization of Mechanocatalytically-Formed Carbonaceous Films on Nanocrystalline Pt$_{0.9}$Au$_{0.1}$ Alloy: Insights into Chemistry, Structure, and Friction Behavior, *Nicolas Molina, C. Edwards,* The University of Texas at Austin; *T. Babuska, J. Curry, F. DelRio,* Sandia National Laboratories; *J. Killgore,* National Institute of Standards and Technology, Boulder; *H. Lien,* The University of Texas at Austin; *M. Dugger,* Sandia National Laboratories; *F. Mangolini,* The University of Texas at Austin
Nanocrystalline Pt-Au alloys have emerged as a highly promising class of hard and wear-resistant materials with potential application in several fields, including in electrical contacts (EC) and next-generation nanoelectromechanical systems (NEMS). While the mechanocatalytic formation of carbonaceous surface layers at the interface between sliding metallic contacts has been reported in the case of pure Pt (found to decrease adhesion and friction but increase the electrical resistance, resulting in reliability issues when Pt is used in NEMS switches), remarkably little is known about the chemistry, structure, and tunability of these interfacial layers in the case of Pt-Au alloys. In this study, we conducted tribological experiments on a nanocrystalline Pt$_{0.9}$Au$_{0.1}$ alloy in the presence of ethanol (C_2H_6O) or isopropanol (C_3H_8O) vapor (partial pressure ranging from ultra-high vacuum (UHV) to 3 mbar). To gain insights into the chemical nature and structural properties of the mechanocatalytic, carbon-rich films formed on Pt$_{0.9}$Au$_{0.1}$ surfaces, ex-situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling measurements were carried out. Notably, the development of a robust ToF-SIMS characterization methodology integrating molecular formula prediction (MFP) and multivariate statistical analysis (MVSA) allowed for highlighting subtle differences in elements' bonding configuration and functional moieties in the ultrathin carbon surface layers formed on Pt$_{0.9}$Au$_{0.1}$ surfaces, including aromaticity of carbon atoms, hydrogenation, and molecular weight distribution. Our findings, demonstrating the intricate interplay between mechanocatalytic film formation, the nature of the organic gas environment, and gas pressure, not only advance our understanding of the tribological processes occurring on Pt-Au alloys, but also provide guidelines for tailoring the mechanocatalytic formation of carbonaceous surface layers and modulating their tribological behavior by rationally varying the organic gas environments and pressure. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

AS-ThP-15 Quantification of Surface and Subsurface Structures of Complex Thin Films with LEIS, XPS and Sputter Depth Profile Simulations, *M. Valtiner, Camil Bocaniciu, J. Pichler, A. Celebi,* TU Wien, Austria
Sputter depth profiling is an established technique to analyze surface and subsurface concentration profiles on various surfaces using different techniques such as XPS or AES. However, during sputtering both preferential sputtering as well as atomic intermixing do interfere with a detailed evaluation of surface and subsurface species. Here we show how a combination of Low Energy Ion Scattering and angle resolved XPS can reveal accurate depth distributions with high vertical profile resolution. Therefore, we also performed Monte Carlo based simulations of the sputtering processes, and fitted these to elemental distributions measured by LEIS and XPS during sputtering. We can show that our approach allows us to reconstruct accurate surface and subsurface distributions in complex materials and thin films including series of stainless steels, high entropy alloys as well as plasma etched silicon wafers with varying oxide thicknesses. Based on our approach a detailed elemental profiling with close to mono layer elemental distribution accuracy is possible. This is interesting for various fields including catalysis, corrosion as well semiconductor processing.

AS-ThP-16 Multimodal Characterization of Copper Hydroxy Chloride for Advanced Thermochemical Energy Storage Applications, *Kavin Chakravarthy Thangaraj, X. Zhang,* Washington State University, US; *V. Prabhakaran, V. Murugesan, A. Karakoti,* Pacific Northwest National Laboratory
Developing efficient energy storage systems is paramount for achieving carbon neutrality and maximizing the use of renewable energy sources. Thermochemical energy storage systems (TCES), a distinct subclass of thermal energy storage systems (TES), have gained significant attention for their ability to store energy from intermittent energy sources like solar and wind. TCES work by storing and releasing thermal energy through processes such as adsorption, absorption, or chemical reactions. Salt hydrates are commonly studied for TCES applications due to their high energy density, cost-effectiveness, and eco-friendly qualities. However, challenges arise from the limited availability of suitable salt hydrates for specific uses and the need for additional materials like thermal conductive additives and phase stabilizers for optimal performance. Additionally, multimodal and in-situ characterization of TCES materials is required to identify the material degradation modes during energy storage and release cycles, which will enable the design of novel, better-performing materials.

To address these challenges, we explored the potential of copper hydroxy chloride (CHC), a double anion salt of copper, for TCES applications. The insolubility of CHC in water reduces deliquescence-associated performance degradation over extended cycling periods compared to other salt hydrate systems. Our study encompassed a multimodal evaluation of CHC for the application in TCES by analyzing its dehydration and hydration cycling behavior. Specifically, we utilized in-situ X-ray diffraction (XRD) and in-situ X-ray photoelectron spectroscopy (XPS) to discover a stagewise decomposition of CHC at different temperatures during its dehydration, resulting in the release of water and chlorine byproducts. By employing methods such as thermogravimetry- differential scanning calorimetry (TG-DSC), and a calorimeter paired with a humidity generator, we evaluated the temperature range suitable for hydration and dehydration of CHC, the associated heat changes (enthalpies) and the temperature range where the reversibility of reactions could be preserved. The multimodal and in-situ methods developed are largely applicable to other TCES materials for identifying the hydration, dehydration, and degradation mechanisms of salt hydrate-based materials and evaluating their promise as thermal energy storage systems, eventually contributing to the broader goal of sustainable and efficient energy storage.

AS-ThP-17 Observation of Multiple Flat Bands and Van-Hove Singularities in a Distorted Kagome System NdTi$_3$Bi$_4$, *Mazharul Islam Mondal, A. Sakhya, M. Sprague,* University of Central Florida; *B. Ortiz,* Oak Ridge National Laboratory, USA; *M. Matzelle,* Northeastern University, US; *N. Valadez, I. Bin Elius,* University of Central Florida; *B. Ghosh, A. Bansil,* Northeastern University, US; *M. Neupane,* University of Central Florida
Kagome materials have attracted enormous research interest recently owing to their diverse topological phases and manifestation of electronic correlation due to their inherent geometric frustration. Here, we report the electronic structure of a distorted Kagome metal NdTi$_3$Bi$_4$using a combination of angle-resolved photoemission spectroscopy (ARPES) measurements and density functional theory (DFT) calculations. We discover the presence of two "flat" bands which are found to originate from the Kagome structure formed by Ti atoms with major contribution from Ti $d_{xy}$and Ti $d_{x^2-y^2}$ orbitals. We also observed multiple van Hove singularities (VHSs) in its electronic structure, with one VHS lying near the Fermi level (E_F). Our calculation indicates the presence of a bulk Dirac cone at the Γ point and a linear Dirac-like state at the K point with its Dirac node located very close to the E_F. Our findings reveal NdTi$_3$Bi$_4$as a potential material to understand the interplay.

AS-ThP-18 Quantitative Analysis for Chromium Oxidation, *Milton Vazquez-Lepe,* University of Guadalajara, Mexico; *A. Herrera-Gomez, O. Cortazar,* CINVESTAV-Queretaro, Mexico; *S. Aguirre,* CIMAV-Monterrey, Mexico; *C. Weiland,* Brookhaven National Laboratory
The background in X-ray photoelectron spectroscopy, is formed from inelastic scattering. To evaluate oxide states for quantification, Tougaard background and Shirley background intensity must assessed appropriate. The experimental background can be calculated with several methods with different contributions for the total area. For determination of composition,

the Cr3s, Cr3p and O2s core levels were analyzed from 400 eV to 900 eV of emission source. These intensities were modified to evaluate the appropriate chemical quantification. Also, varying the photon energy applied, Shirley intensity is changing and was incorporated using the SVSC method that allows for accounting the differences for the assessment.

AS-ThP-19 Temperature Dependency of Doping Silicon with Phosphorus Using Ultra-Thin Films of P-Containing Minerals, *Roman Konoplev-Esgenburg, P. Thissen,* KIT, Germany

This work explores a novel approach using ultra-thin films of P-containing minerals which are Hydroxyapatite ($Ca_5(PO_4)_3OH$), Struvite ($MgNH_4PO_4*6H_2O$), and Monetite ($CaHPO_4$) and we expect high-temperature dependency of doping process due to different decomposition profiles. Thin films were prepared via a tethering by aggregation and growth method and subsequently processed by spike annealing. Minerals offer a large variety of materials that can be used in this doping process.

In-situ infrared (IR) spectroscopy reveals the decomposition of a mineral and its intermixing with the native silicon oxide at low temperatures (for Hydroxyapatite at 200°C). This process involves the migration of phosphate through the native oxide layer driven by a phase transformation into a more stable thermal oxide. Ultimately, the diffusion of phosphorus into the underlying oxide-free silicon layer is observed (for Hydroxyapatite at 700°C). By combining in-situ IR with electrical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS), the measurements allow us to conclude the following process. Firstly, the transport of phosphorus through the silicon oxide barrier and subsequent diffusion of phosphorus within the oxide-free silicon layer. Finally, the phosphorus concentration profile was confirmed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

To further explain and investigate experimental doping processes using thin films of P-containing minerals, mineral interfaces were modeled and DFT calculations were performed. The Nudged Elastic Bands (NEB) method provides us with the mechanism of phosphorus transport. Vibrational frequencies were calculated to correlate them with IR spectroscopy. Additionally, the DFT methods helped us optimize each corresponding doping process from the electrical perspective: electronic band structure, and pinned impurity levels that result in charge carrier trapping as each interface necessarily displays different electrical properties.

AS-ThP-20 Coincident XPS, Raman and SEM Analysis of Additive Manufacturing Devices, *Mark Isaacs,* University College London, UK; *D. Morgan,* Cardiff University, UK; *A. Leung, K. Kim, S. Bhagavath,* University College London, UK

Additive manufacturing processes are a keenly investigated methodology for the preparation of sophisticated devices for a multitude of technologies, including catalysis, electronics and sensors. At the heart of the functionality of these systems often lies the surface and interfacial properties of the resultant materials. In order to develop a holistic understanding of the eventual nature of these devices, and for the complete assessment of favourable printing parameters, oftentimes a multitude of characterisation methods is required. Coincident analysis of surface analysis techniques such as XPS, SEM, REELS and UPS - along with additional complementary techniques such as Raman spectroscopy - permits a wealth of understanding around the physical, chemical and electronic properties of printed tracks and leads to an overall optimisation of system parameters to develop highly specific and tuneable materials. In this work, we study a range of printing parameters for the deposition of MoO_3 tracks onto a copper support - a material with promising applications in the electrocatalytic reduction of CO_2. Using XPS, linked with SEM/EDX via a CISA (Correlative Imaging and Surface Analysis) Workflow and Raman spectroscopy, we investigate a range of printing parameters in order to determine favourable properties for the creation of phase interfaces understood to be active for electrocatalytic applications. Chemical and electronic properties are also investigated through complimentary surface analysis by REELS and UPS.

AS-ThP-21 Investigation into the Blackening of Lead-Glazed Ceramic Objects, *Alexandra DiCarlo, A. Walker,* University of Texas at Dallas

Lead glaze on earthenware undergoes blackening in anaerobic environments such as those found in cesspits and canals. The blackening effect is attributed to the formation of black lead(II) sulfide within the glaze. However, the degradation process is not well understood; degraded glazes exhibit not only black colors but also red and orange colors. In this study, five lead-glazed ceramic pieces excavated from the canals of Amsterdam were analyzed using optical microscopy, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy to investigate the chemical and physical properties of the aged glazes. Each ceramic piece exhibited different levels of degradation from fully black to off-white. Optical images revealed that the most visibly damaged objects have rougher surfaces and crystals growing in cracks of the glaze. Raman spectra and XPS data indicate that the objects share many of the same components, including lead oxides, tin(II) oxide, and silicon dioxide. Surprisingly, other lead compounds that are not known to be ingredients of glaze are also present, including lead(II) carbonate, lead(II) sulfide, and lead(II) sulfate. To determine if a correlation between the chemical compositions and the perceived colors of the objects existed, principal component analysis (PCA) was conducted, but there does not appear to be any strong correlations. This is likely due to the limited number of samples investigated.

AS-ThP-22 A Computational Approach to Model Radical Formation in Low Temperature Plasma Generated from Pentane and Acrylic Acid as Precursors, *Mackenzie Jackson, K. Closser, M. Hawker,* California State University, Fresno

Plasma enhanced chemical vapor deposition (PECVD) is an ideal method to change the chemical properties of surfaces without affecting bulk properties. In the literature, PECVD in conjunction with computational studies primarily focus on coating semiconductors with organometallic and semimetal-based films. Many PECVD systems utilize organic precursors, especially to modify surfaces to interface with biological environments. This research seeks to fill the gap by studying thin films deposited using organic plasma precursors, specifically acrylic acid and pentane. Computational modeling of these organic precursors will help in understanding key characteristics of the deposition of the thin film via the thickness of the film, deposition rate, and the chemical composition of the film.

This study models the precursors– acrylic acid and pentane– using computational chemistry. Classical density functional theorem (DFT) functions were used to examine geometries, frequencies, and energies of neutral radicals and cations formed during precursor ionization. Data were obtained using the quantum chemistry program Q-Chem with the methods B3LYP and CCSD(T) along with the 6-311(2d,2p) basis set. Data were then analyzed to determine the most stable fragments, which were subsequently used to predict species most likely formed plasma-polymerized films. Preliminary data shows the most energetically favorable way to break both precursor molecules was between the C2 and C3 bond. The least energetically favorable spot for the split on pentane occurred between the H and C3 bond while acrylic acid required the most energy to separate the O from the C3 carbonyl. Currently, data obtained is limited to the energetics of the split and recombination of pentane and acrylic acid separately. In future work, the fragments from pentane and acrylic acid will be combined to determine the lowest energy co-polymers between the two, in conjunction with experimental surface measurements, and will be used to develop a machine learning model to predict the properties of the co-polymers these compounds form.

AS-ThP-23 Improving Field Emission Device Performance by Optimizing the Emitter Shape, Dimension, and Space Distribution Based on Finite Element Analysis, *Jaden Lu, O. Lu,* Hamilton High School

Cold cathode field emission devices have attracted much attention due to its unique properties such as high current density and low working temperature. To gain strong field enhancement factors, the field emitters with high aspect ratio are widely used. However, these sharp tips have a great disadvantage. The strong emission current passing the sharp tips will generate very high temperatures. The tips will melt or crack under such high temperatures, and its morphology will change dramatically. This will result in unstable emission current and cause device failure.

In this research, Finite Element Analysis software COMSOL was used to simulate the field emission device. Various emitter shapes and dimensions were simulated to compare the emission current and resultant temperature increase of the emitter. The field emission failure mechanism will be investigated based on the simulated data. An existing failure model proposed by other researchers is the melting of materials under local high temperatures. However, the high temperature will also cause extra strain due to thermal expansion. The material will crack if the thermal strain is over a certain limit. COMSOL simulation will validate these models. On the other hand, since the practical field emission device is composed of arrays of many emitters, this work also studies the impact of space distribution on

the field emission device performance. Different emitter array structures were simulated to understand the electric field distribution.

To mitigate the impact of high temperature generated by emission current, several solutions were proposed and evaluated by COMSOL simulation. The first solution is to dope the materials to reduce its electrical resistivity. This will control the Joule heat from high emission current. Doping impact and surface modification are simulated to study the bandgap change, quantum tunnel efficiency, and current density. The second solution is to optimize the emitter cross section area to reduce the Joule heat. It is known that a higher cross section area will result in lower electric resistance and thus decrease the Joule heat. This solution will require the balance of electric resistance and aspect ratio of the emitter to achieve sufficient emission current under relatively low bias voltage. The third solution is to find different emitter shapes to achieve high thermal conductivity. The generated heat can be quickly transported to the surrounding environment and therefore the damage to the field emitters can be reduced. Based on this research, a stable field emission device structure was proposed with optimal emitter shape, dimension, and space distribution.

AS-ThP-24 Metallic 3D-Printing Materials Analysed by Secondary Ion Mass Spectrometry, *A. Akhmetova, D. Breitenstein,* Tascon GmbH, Germany*; M. Glauche,* implantcast GmbH, Germany*; M. Kluge,* Fraunhofer Research Institution for Additive Manufacturing (IAPT), Germany*; E. Tallarek, Reinhard Kersting, B. Hagenhoff,* Tascon GmbH, Germany

In contrast to traditional manufacturing processes, 3D printing offers advantages in terms of the achievable complexity of the printed parts and their individuality. Typically, 3D printing is said to be more efficient in terms of materials, which can go hand in hand with cost savings.

3D printing is now used not only for polymers, but also for metals. Spherical metal powders are melted in a targeted manner using either an electron or a laser beam. The remaining powder can be separated and fed back into the printing process.

However, reusing the powder in metal 3D printing is not yet possible indefinitely: the powders typically show signs of ageing after several printing cycles, meaning that the quality of the 3D print suffers. In practice, the powders therefore have to be disposed of after several printing cycles.

There are indications that these ageing processes correlate with changes in the surface properties of the metal powders used. For a better understanding of powder aging and related printing processes, it is therefore important to study defects in 3D-printed samples as well as raw metal powders with suited analytical methods. In the present study this is performed by means of Secondary Ion Mass Spectrometry (SIMS).

AS-ThP-25 Advanced Automated Workflows and Elemental Identification for Non-Expert XPS Analysis, *Jonathan Counsell, L. Soomary,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc., UK*; K. Macak,* Kratos Analytical Limited, UK, Slovakia*; K. Good,* Kratos Analytical Limited, UK

A novel peak identification (peak-ID) algorithm has been developed to significantly improve data-dependent acquisition (DDA) in X-ray photoelectron spectroscopy (XPS). Traditional XPS analysis relies heavily on manual peak assignment, which can introduce errors and inconsistencies, particularly in complex or noisy spectra. The new peak-ID algorithm addresses these challenges by automating the detection and classification of spectral peaks, offering a more precise and consistent approach to XPS analysis.

This algorithm enhances the limit of detection by accurately identifying low-intensity peaks that may be overlooked by conventional methods, enabling the detection of trace elements and subtle chemical states with higher confidence. By automating the peak identification process, the algorithm minimizes human error in peak assignment, ensuring more reliable data interpretation. The integration of this peak-ID system into DDA workflows allows for real-time optimization of data acquisition parameters, focusing on regions of interest in the spectrum and thereby improving the overall efficiency and effectiveness of the analysis.

Additionally, this approach reduces the risk of missing critical information by dynamically adjusting the acquisition strategy based on the detected peaks. The algorithm's ability to handle complex spectra with overlapping peaks further enhances its utility in diverse applications, from materials science to surface chemistry. Overall, the new peak-ID algorithm represents a significant advancement in XPS technology, offering improved sensitivity, accuracy, and efficiency in automated surface analysis.

AS-ThP-26 Online Accurate Intensity Calibration for X-ray Photoelectron Spectroscopy Instruments, *Alexander Shard, B. Reed, S. Spencer, D. Sundaram, T. Fielder, C. Lambie, D. Melling,* National Physical Laboratory, UK

Calibration of the intensity scale in X-ray Photoelectron Spectroscopy (XPS) is important to ensure that quantitative data are reliable, reproducible, and replicable. In the 1980's the National Physical Laboratory established a system for the accurate intensity calibration of electron spectrometers.[1] The method employs accurate reference spectra from clean copper, silver and gold foils suitable for any instrument geometry. The approach underpins, and is more accurate than, the calibration procedure using a secondary reference material, low density polyethylene[2, 3] which has now been adopted as international standard ISO 5861. The software originally developed in the late 1990's to disseminate the calibration procedure no longer works on modern computers and had rather stringent data input requirements as well as a slow operation. NPL have updated the method and have implemented it on a web-based portal. The new procedure is approximately 100 times faster than the previous software and can handle up to 21 files input simultaneously, enabling seven instrument modes to be calibrated in a single five-minute session. There are no longer any requirements for files to be entered sequentially in single block VAMAS format, nor for there to be a specified energy step size. The calibration results and associated uncertainties are checked, certified, and digitally delivered to enable analysts to have evidence of calibration as part of their quality system.

1. M. P. Seah, J. Electron Spectr. Rel. Phenom. **71** (3), 191-204 (1995).
2. B. P. Reed et al, J. Vac. Sci. Tech. A **38** (6) (2020).
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AS-ThP-27 Sublime cryo-XPS, *David Surman,* Kratos Analytical Inc*; J. Counsell,* Kratos Analytical Limited, UK

Cryogenic X-ray photoelectron spectroscopy (cryo-XPS) is an advanced analytical technique that offers unparalleled insights into the surface chemistry of materials at cryogenic temperatures. This method is particularly advantageous for analyzing delicate and volatile samples that might otherwise degrade or alter under standard conditions. One of the significant challenges in cryo-XPS is the formation of frost on the sample surface, which can obscure the true surface chemistry and lead to erroneous interpretations. In this study, we present a novel method for mitigating this issue by employing gentle warming to selectively remove the frosting while preserving the integrity of the underlying frozen surface.

The process begins by cooling the sample to cryogenic temperatures, typically below 120 K, where frost naturally forms due to the condensation of ambient moisture. Rather than allowing this frost to interfere with XPS measurements, we implement a controlled warming protocol. This careful warming is monitored using precise thermocouples and controlled heating elements, ensuring that the sample remains in a stable cryogenic state during the entire procedure.

Our method was tested on various salt solutions known for their sensitivity to temperature and environmental conditions. The results demonstrated a significant improvement in the quality and accuracy of the XPS spectra obtained post-frost removal. The true chemical states and compositions of the samples were revealed, providing deeper insights into their surface properties.

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