Applied Surface Science
Room Central Exhibit 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.

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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, Fe2O3 is the oxide composition.

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[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.

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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-6 Multitechnique Analysis of Ultrathin Films for the Photocatalytic Production of Sustainable Aviation Fuels*, **Mark Isaacs,*** University College London, UK*; L. Durndell,* University of Plymouth, UK*; C. Parlett,* University of Manchester, UK*; C. Drivas,* Cardiff University, UK

In the search for technologies by which to reduce the overreliance on traditional fossil fuel based transport, the utilisation of biomass derived feedstocks to produce aviation fuels represents an exciting avenue for minimising the carbon footprint of global travel. Developing new materials, and improving and optimising the performances and activities of these materials requires a fundamental understanding of the physical, chemical and electronic properties down to the nano-domain - particularly when considering some of the more sophisticated synthetic protocols employed in advanced nanomaterials such as surface modifications vie ultra-thin films, galvanostatic interaction depositions, formation of Schottky junctions and more. X-ray photoelectron spectroscopy (XPS), and surface science in general, is ideally suited to extracting directly relevant information about these properties and, when combined in a coincident manner, develop a completely holistic understanding of how nanomaterial synthesis parameters may be controlled to imbue fine control over the resultant properties - and understand how these may impact upon catalytic activities. In this work, we investigate a series of ultra-thin layers of titania deposited onto the surface of a high surface area silica and correlate material properties with the catalytic performance in the acetalisation of furfural into 2,5-Bis(2-furylmethylene) cyclopentanone. Comprehensive chemical, electronic and structural analysis is performed using a combination of correlative XPS, REELS, UPS, Raman and ISS, and mapped with catalytic performance in the presence and absence of stimulating light.

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-10 Misunderstandings in Field Electron Emission Theory: The Great Fowler-Nordheim Hoax*, **Richard Forbes,*** University of Surrey, UK

Field electron emission (FE) is electrostatic-field-induced electron emission from a material surface. Many vacuum-based technologies involve FE. This Poster corrects a widely held misconception about FE theory.

In 1928, *qualitatively* correct theories of FE as wave-mechanical transmission were given by Oppenheimer and by Fowler and Nordheim (FN), using different approaches. But FN also used Fermi-Dirac statistics to explain weak FE temperature dependence near 300 K. Thus, FN get credit for explaining FE. In fact, FN's paper is flawed both theoretically and numerically. Image-charge effects were much under-estimated and there was a separate numerical error by about 10^{15}. The numerical error was corrected by Stern et al. in 1929. The image-charge error was found by Nordheim later in 1928, but he then made a new error when using complete elliptic integrals. Nordheim's mistake was corrected by Burgess, Kroemer and Houston in 1953. In 1956, Murphy and Good (MG) developed revised FE theory that gave much higher current densities (100 times or more) than Stern et al. Unfortunately, many later authors called MG's theory the "Fowler-Nordheim equation".

In the 1990s, interest in displays brought many new researchers into FE. It seems many did not realise that the term "Fowler-Nordheim equation" often referred to the 1956 MG FE equation rather than the 1920s-era equations. More confusion was caused by the use of a simplified ("elementary") version of the 1920s-era equations to extract the electrostatic parameter "field enhancement factor" from experiments. This is now widely done. But if the elementary FE equation is used to predict current densities, or extract emission areas, then errors of order 100 or more arise, as compared with 1956 MG FE theory. Thus, modern FE

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[1] **ASSD Student Award Finalist**

technological literature is highly misleading, especially for non-experts. Hundreds of papers give the elementary FE equation as FE theory, and cite the FN 1928 paper as justification. This paper has over 8000 citations, but few draw attention to its theoretical weaknesses. Hundreds of authors have been "hoaxed" by misleading FE literature, and then perpetuate the hoax.

When developing new types of high-quality electron source, or studying the role of FE in electrical breakdown, it is misleading to publish/use an equation that underpredicts emitter performance by 100 times or more. When extracting emission-area estimates for R&D use, it is unhelpful to use an equation that over-predicts area by 100 times. A good remedy uses a modern version of the 1956 equation, calls it the "Murphy-Good FE equation", and cites a modern FE research handbook.

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-12 XPS Analysis of Plasma Exposed TiB_2 and ZrB_2 Substrates*, Harry Meyer*, *L. Nuckols, C. Parish, J. Rapp,* ORNL

Deuterium and hydrogen plasma exposures were performed on ultra-high temperature ceramics TiB2 and ZrB2 using the PISCES-RF linear plasma device as early screening tests for first wall, plasma facing material applications. These ion plasma exposures were performed using 40 eV ion energies at 240, 525, and 800 ◦C sample temperatures and 90 eV ion energies at 240 ◦C sample temperatures to analyze TiB2 and ZrB2 sputtering and surface morphology evolution behavior. Post-plasma exposure chemistry characterization of the near surface (< 50 nm) region using x-ray photoelectron spectroscopy (XPS) shows transition metal enrichment, indicating boron preferential erosion, and resulting in reduced total sputtering yields compared to predicted assuming stoichiometric sputtering. Transition metal to boron fractions vary with plasma exposure temperature under the 40 eV ion energy exposure at different temperatures; metal enrichment is maximized at 800 ◦C and then minimized at 525 ◦C. Sputtering yield measurements of the 40 eV ion energy plasma exposed samples show that the samples with greater metal surface enrichment have lower sputtering yields, likely due to the rougher surfaces of the more metal-enriched samples leading to higher instances of prompt redeposition processes.XPS data was acquired on the as-exposed TiB2 and ZrB2 samples.Depth profiles were then done to track the amounts of T (or Zr) and B as a function of Ar-ion sputter depth.Data was finally acquired on the well sputtered sample surfaces.This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

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*, **Markus Valtiner**, C. 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 $NdTi_3Bi_4$*, **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 $NdTi_3Bi_4$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 $d_x2-{}_y2$ 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 $NdTi_3Bi_4$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.

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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.

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