

Wednesday Afternoon, November 6, 2024

Applied Surface Science

Room 117 - Session AS-WeA

Advanced Materials and Methods

Moderators: Tanguy Terlier, Rice University, Julia Zakel, IONTOF GmbH, Germany

2:15pm AS-WeA-1 Ion Migration and Chemical Phenomena in Functional Materials: Correlative Studies via Combined AFM/ToF-SIMS Approach, Anton Ievlev, Oak Ridge National Laboratory

INVITED

The performance of various electronic devices is defined by the delicate interplay of electrical response and charge carrier migration at the nanoscale. Although physical behavior and macroscopic functional response of these materials is well established, intrinsic chemical phenomena associated with ionic motion or localized electrochemical reactions can dramatically alter their behavior and thus restrict area of utilization. Over the last decade, advancements in development of novel nanoscale characterization tools such as atomic force microscopy (AFM) have revolutionized our understanding of the electrical and mechanical response of materials; however, *dynamic* electrochemical behavior and ion migration remain poorly understood. Recently time-of-flight secondary ion mass spectrometry (ToF-SIMS) has proven to be effective tool for characterization of static chemical states in energy materials. However, its application to study of dynamic electrochemical processes still requires development.

Here we introduce approach based on combined AFM/ToF-SIMS approach for correlated studies of the dynamic chemical phenomena on the nanoscale in operando conditions. Being used for characterization of the range of electronic materials, including ferroelectrics, photovoltaics and memristors it allowed direct observation of the ionic migration within the device in externally applied electric fields, which is important for fundamental understanding of the material functionality. Altogether, developed approaches enable direct characterization of interplay between chemical and functional response in variety of materials, which aids in the development and optimization of novel devices and applications.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility and using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

2:45pm AS-WeA-3 Elemental and Chemical Quantification of Porous Transport Electrodes with X-Ray Photoelectron Spectroscopy Analysis and Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy, Lonke van Eijk, Colorado School of Mines; J. Foster, Colorado School of Mines, USA; S. Khandavalli, National Renewable Energy Laboratory; L. Ding, University of Tennessee, Knoxville; G. Stelmachovich, Colorado School of Mines, USA; S. Mauger, National Renewable Energy Laboratory; F. Zhang, University of Tennessee, Knoxville; A. Paxson, Plug Power; S. Pylypenko, Colorado School of Mines, USA

Optimization of proton exchange membrane water electrolyzers (PEMWEs) is essential to ensure reliable hydrogen generation and societal transition towards greater hydrogen energy use. Further improvements are crucial for facilitating the widespread adoption of hydrogen as a sustainable energy source. Various avenues are under exploration to advance PEMWEs further, aiming for increased activity and stability of catalysts, alongside the optimization of catalyst layer (CL) structure. This work focuses on the development of porous transport electrodes (PTEs), consisting of an iridium oxide-based catalyst layer and a titanium-based porous transport layer coated with a platinum protective layer. This project explored several CL deposition methods, including airbrush, rod coating, ultrasonic spray coating, and electrodeposition, to achieve homogeneous CL coatings and control of catalyst loadings. Additionally, post-treatments of PTEs were explored to elucidate the interplay between activity and stability of CLs and further optimize the performance.

The main goal of this study was the development of quantitative metrics that can be used for comparative studies of the quality of CL coatings and their performance. The first part of my talk will discuss scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) analysis of a series of PTEs produced with various routes. SEM-EDS was used to assess the elemental composition and the distribution of elements of interest. In addition to qualitative assessment of SEM-EDS images, this study also implemented quantitative metrics based on Pt:Ir ratios. The

implementation of proper characterization of these PTEs can help aid future decisions on which fabrication and processing parameters should be used to achieve coatings with desired quality and loadings. This approach can also be used for quality control, enabling quick screening of commercially produced samples. The second part of my talk will discuss the X-ray Photoelectron Spectroscopy (XPS) data analysis for chemical analysis of PTEs annealed under various environmental conditions and temperatures, with the goal of elucidating the impact of these parameters on material properties and electrochemical performance. This talk will discuss results and challenges associated with the analysis of Ir-based materials and will highlight trends between several quantitative metrics derived from XPS data and their correlations with electrochemical parameters. The findings not only contribute to advancements in PEMWE technology but also underscore the importance of the identification of simple metrics that can be used for trend identification in complex datasets.

3:00pm AS-WeA-4 Comprehensive Characterization of Porous Transport Layers and Porous Transport Electrodes with Time-of-Flight Secondary Ion Mass Spectrometry, Genevieve Stelmachovich, L. van Eijk, J. Foster, Colorado School of Mines; L. Ding, University of Tennessee, Knoxville; S. Ware, J. Young, National Renewable Energy Laboratory; F. Zhang, University of Tennessee, Knoxville; A. Paxson, Plug Power Inc.; G. Bender, National Renewable Energy Laboratory; D. Cullen, Oak Ridge National Laboratory; S. Pylypenko, Colorado School of Mines

Proton Exchange Membrane Water Electrolysis (PEMWE) is a promising technology towards the realization of the hydrogen economy. PEMWE components include the porous transport layer (PTL), a sintered or felt titanium material, and the adjacent catalyst layer (CL) which is typically made with IrO_x or IrRuO_x catalyst. Recent advancements in manufacturing have pushed towards the fabrication of porous transport electrodes (PTEs), where the anode CL is directly coated onto the PTL. To mitigate degradation of the PTL and improve the interface between CL and PTL, PTLs are typically coated with a thin protective coating, usually Pt. This leads to a complex layered PTE structure that consists of catalyst layer, protective coating, and porous transport layer (IrO_x/Pt/Ti or IrRuO_x/Pt/Ti) and is difficult to characterize.

Previously, we have demonstrated Time of Flight Secondary Ion Mass Spectrometry (TOF SIMS) as a powerful characterization technique for the qualitative and comparative characterization of PTLs, enabling the assessment of the interface between protective coating and PTL. Further, we focused on analysis of protective coatings with a focus on their thickness. We correlated TOF SIMS data and Scanning Transmission Electron Microscopy (STEM) measurements to demonstrate that TOF SIMS can be used to reliably compare coatings with different thicknesses despite the complex morphology of the substrate. More recently we used TOF SIMS to characterize a series of PTEs made with electroplated IrRuO_x catalyst that underwent various post-treatments. A combination of spectroscopy, imaging, and depth profiling analysis was utilized to identify chemical and spatial differences. This data was combined with Scanning Electron Microscopy Energy Dispersive X-Ray Spectroscopy (SEM-EDS), STEM, and X-Ray Photoelectron Spectroscopy (XPS) analysis to highlight the complementary nature of TOF SIMS analysis and demonstrate the need for comprehensive characterization with multiple techniques.

3:15pm AS-WeA-5 Characterization of the Nanostructure and Composition of Mollusc Shells Using Advanced Spectroscopic and Imaging Techniques, David Morgan, Cardiff University, UK

Biomineralization is an important field, informing researchers across many disciplines, on materials design, understanding of evolution and the development of tissue-engineering. Molluscs biomineralize to form shells as a means of protecting their internal soft tissues and these strong shells have led to molluscs becoming the second largest invertebrate phylum with over 70,000 species.

These shells are organo-mineral composite structures consisting of two key components - an inorganic carbonate mineral and organic macromolecules (e.g. proteins, polysaccharides). This complex structure imbues them with enhanced mechanical properties, such as high strength and fracture toughness. In recent years, much attention has been focused on the nacreous shell structure to replicate materials with similar strengths and toughness. To date, most research papers have focused on the microstructures of these shells, little work has been done on their nanostructure which represents a key gap in our knowledge of biomineralization since amorphous calcium carbonate nanostructures form the first building blocks of these hierarchical structures.

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The presented work focuses on the intricate nanostructure and composition of the Fluted Giant Calm (*Tridacna squamosa*) by means of Photo-induced Force Microscopy (PiFM) and X-ray Photoelectron Spectroscopy (XPS). We show that XPS unequivocally confirms the presence of calcium (Ca) and magnesium (Mg) within the z-axis of the shell matrix, whilst, PiFM unveils a multifaceted composition, indicating that the shell comprises a mixed-phase carbonate structure, intricately woven from both structured and amorphous aragonite and magnesite. Notably, PiFM analysis reveals a structural distinction between the Inner and Outer Shell layers, with the outer layers displaying distinct "zebra stripe" patterns, denoting magnesite and dolomite-like bonding that traverses the aragonite structure. This study significantly contributes to advancing our comprehension of mollusc shell structure and composition.

3:30pm AS-WeA-6 Development of Best Practices for Cryo-XPS – Opening the Possibility to New Sample Analysis and Paving a Route to Standardization, K. Zahra, *Liam Soomary*, Kratos Analytical Limited, UK; C. Moffitt, D. Surman, Kratos Analytical Inc.; J. Counsell, Kratos Analytical Limited, UK

Conventional x-ray photoelectron spectroscopy (XPS) has typically limited samples to solids, powders, and thin films due to the ultra-high vacuum (UHV) requirements of analysis. This has constrained the utilization of XPS in various industries (e.g. biological/ medical and battery manufacturing), due to the preparation requirements to create vacuum compatible samples often resulting in analysis in non-native environments. Developments in near-ambient pressure (NAP-XPS) and frozen hydrated sample (cryo-XPS) analysis is beginning to bridge these gaps. NAP-XPS systems are widely available at synchrotron facilities, with commercial instruments also on the market. However, beamtime is highly competitive and commercial instruments are currently expensive.

Previous comparisons in the literature between the two methods have shown both give comparable data [1]. Still the ability to maintain UHV conditions using cryo-XPS minimises surface contamination and provides higher signal intensity, therefore enabling shorter acquisition times. Cryo-XPS is also an accessory added to conventional XPS making it a cost-effective option.

Rate of cooling is a major consideration in cryo-XPS. Slow rates of freezing result in fewer nucleation sites, thus larger crystals, which cause cellular damage. Flash-freezing is essential to produce vitreous (amorphous, glass-like) ice, preventing crystal formation. In biological and medical research this preserves cellular structures and maintains a near-native state. It also preserves compounds, avoids surface restructuring, and minimises surface degradation. After vitrification, sample temperatures need to remain below -137 °C to prevent devitrification [2]. Thus, sample transfer between the load-lock and analysis chamber must be fast and dependable.

In this talk we hope to provide industry relevant guidelines for sample preparation with a focus on reproducibility using cryo-XPS. We will also demonstrate how layered analysis is achieved when cryo-XPS is coupled with Gas Cluster Ion Source (GCIS) etching to delve deeper into the surface. Finally, we will comment on directions for future improvements in the technique.

[1] M. Kjaervik et al., Comparative Study of NAP-XPS and Cryo-XPS for the Investigation of Surface Chemistry of the Bacterial Cell-Envelope, *Front. Chem.*, (2021) 9:666161. DOI: 10.3389/fchem.2021.666161

[2] G. Weisenberger et al., Understanding the invisible hands of sample preparation for cryo-EM, *Nat. Methods*, (2021) 18:5. DOI: 10.1038/s41592-021-01130-6

4:15pm AS-WeA-9 ASSD Student Award Finalist Talk: 3D ToF-SIMS Imaging of Polyethylene Oxide-Lithium Nitrate Electrolytes in Lithium Ion Batteries, *Reyhane Shavandi*¹, University of Illinois Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is increasingly used to reveal three dimensional atomic and molecular distributions in the solid-electrolyte interface (SEI) of lithium ion batteries [1,2]. Solid electrolytes were previously sandwiched between lithium foil and copper electrodes, subjected to charge-discharge cycling until electrical failure, then lithium dendrites responsible for failure were detected by post-mortem ToF-SIMS analysis [3]. However, the requisite mechanical removal

of the lithium foil prior to ToF-SIMS analysis can inadvertently remove some of the SEI. An alternate strategy was pursued here in which the lithium foil was replaced with thin layers of lithium evaporated *in vacuo* [4], allowing ToF-SIMS to follow the reaction of metallic lithium with the electrolyte. A micrometer-thick solid electrolyte composed of polyethylene oxide (~600 kDa) and lithium nitrate was slot dye coated onto a copper substrate and compared by ToF-SIMS with the same samples on which 10 or 100 nm thick layers of lithium were evaporated. 30 keV Bi³⁺ primary ions from a liquid metal ion gun were used to collect positive ion spectra during simultaneous sputtering with a 10 keV argon gas cluster ion beam (IONTOF M6, Münster, Germany). The depth profiles for NO₂⁺ representing the lithium nitrate salt, C₂H₅O⁺ representing polyethylene oxide and Cu₃⁺ representing the copper electrode indicated that the addition of lithium increased the total fluence of argon cluster ions through the solid electrolyte. A limited number of negative ion spectra were recorded that showed NO₂⁻ and Cu₃⁻ following similar trends as in their positive ion counterpart spectra. However, high NO₂⁻ signals persisted after the Cu₃⁻ signals leveled off and changes were observed in copper cluster secondary ions with lithium addition. These effects are discussed in terms of cluster ion-induced mixing or substrate roughening, and the higher sputtering efficiency expected for the polyethylene oxide and lithium nitrate compared to the copper substrate.

1. T. Lombardo, M. Rohnke, et al., *J. Vac. Sci. Technol. A* **41** (2023) 053207. <https://doi.org/10.1116/6.0002850>

2. Q. Ai, J. Lou, et al., *ACS Energy Lett.* **8** (2023) 1107. <https://doi.org/10.1021/acseenergylett.2c02430>

3. M.J. Counihan, S. Tepavcevic, et al., *ACS Appl. Mater. Interf.* **15** (2023) 26047. <https://doi.org/10.1021/acsam.3c04262>

4. M. Counihan, S. Tepavcevic, et al., *ACS Appl. Mater. Interf.* **15** (2023) 26047. <https://doi.org/10.1021/acsam.3c04262>

4:30pm AS-WeA-10 Understanding the Impacts of Battery Electrode Manufacturing Processes through Surface Characterization Techniques, *Mikhail Trought*, T. Kravchuk, S. Peczonczyk, A. Straccia, M. Nichols, Ford Motor Company

The automotive industry has collectively adopted the shift towards manufacturing lithium (Li)-ion battery powered electric vehicles (EVs) to mitigate the environmental impacts of internal combustion engine vehicles, and to meet the evolving government regulations. Manufacturing of Li-ion batteries, and in particular their electrodes, is multifaceted and consists of multiple process steps that can affect the chemical and physical properties of the battery materials, which directly influences the battery's performance. In this study, we have characterized model solvent-based Li-ion battery electrodes: NMC-based cathodes with polyvinylidene fluoride (PVDF) binder and graphite-based anodes with carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) binders. The effects of the drying and calendaring manufacturing processes on the chemical properties and morphology were studied. X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) were used to assess the chemical composition of these battery materials after drying. In parallel, atomic force microscopy (AFM) was used to assess the battery electrode's morphology after drying and after exposure to mechanical stimuli similar to that of the calendaring process. The quality of the battery electrode is highly dependent on manufacturing processes; characterization techniques need to be implemented to understand how these processes affect the electrode and how that ultimately affects the battery's performance.

4:45pm AS-WeA-11 Characterization of Sodium Ion Batteries - from Postmortem to Operando, *Marcus Rohnke*, T. Ortman, D. Schäfer, J. Janek, Justus Liebig University Giessen, Germany

INVITED

Lithium-ion batteries (LIBs) have been at the forefront of energy storage technology since the early 1990s due to their relatively high energy density (260 Whkg⁻¹), reasonable cost (\$153/kWh), and long lifespan.[1] However, the high demand, lack of raw material availability, poor ecological, political and working conditions in the mining countries require new battery concepts. Despite their lower energy density (~150 Whkg⁻¹) compared to LIBs, sodium ion batteries (SIBs) appear to be an interesting alternative, especially for non-portable applications where weight is secondary. SIBs could be used for stationary storage of excess energy from renewable sources such as wind or solar power. Moreover sodium is the 6th most abundant element on earth and is more evenly distributed throughout the globe than lithium.

Researchers around the world are working on concepts for SIBs with liquid and solid electrolytes, so-called solid-state sodium ion batteries.[2] In most

¹ ASSD Student Award Finalist

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cases, the interface properties between the materials used determine the battery kinetics and long-term cycling behavior. Here surface analytical methods such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) or X-ray photoelectron spectroscopy (XPS) play a key role, in combination with 3D analysis and cross-section preparation.[3] They offer the opportunity to learn more about interfacial processes taking place. This knowledge is essential for continuously improving the performance of batteries.

Within this talk we will give insights in our ongoing work on SIBs with liquid as well as solid electrolytes. We will highlight how SIMS, XPS, SEM and TEM can be used in combination with classical electrochemical methods to learn more about electrode and decomposition reactions in SIBs. The first example focuses on the interfacial kinetics in solid state Na batteries with the solid electrolyte NASICON ($\text{Na}_{3-x}\text{Zr}_2\text{Si}_2.4\text{P}_{0.6}\text{O}_{12}$). In the second example classical hard carbon electrodes from electrochemical cells with liquid electrolytes are characterized in 3D with a special focus on the so called solid electrolyte interface (SEI). Here a decomposition layer is formed, which has a significant impact to the cellular kinetics.

Funding was received through POLIS Cluster of Excellence – Post Lithium Storage.

[1] R. Zhao, S. Zhang, J. Liu, J. Gu, *J. Power Sources* **2015**, 299, 557–577

[2] D. Schäfer, K. Hankins, M. Allion et. al., *Adv. Energy Mater.* **2024**, 2302830

[3] T. Lombardo, F. Walther, C. Kern et al., *J. Vac. Sci. Technol. A* **41** **2023** 053207

5:15pm AS-WeA-13 Surface Analysis of Engineered Particles for Improved Battery Performance and Stability, Jennifer Mann, S. Zaccarine, Physical Electronics; I. Oladeji, ULVAC Technologies, Inc.; K. Suu, Ulvac Technologies, Inc., Germany; K. Artyushkova, Physical Electronics

We require next-generation battery materials to achieve optimal energy density, rapid charging capabilities, and extended device longevity, all while maintaining affordability and reliability. Lithium metal batteries present a promising alternative to lithium-ion batteries; however, they encounter stability issues such as unstable solid-electrolyte interphase (SEI) growth and the formation of lithium dendrites. Similarly, cathode materials with high energy density, such as nickel manganese cobalt (NMC), demonstrate stable performance at high potentials but are vulnerable to dissolution within the electrolyte and unstable SEIs. Engineered particles (Ep) offer a solution by stabilizing electrode interactions, thus enhancing battery safety, SEI formation, and overall performance. Nonetheless, batteries are multi-layered, complex systems with numerous components and interfaces, posing challenges to characterization. A comprehensive understanding of the chemical composition, distribution, and morphology of Ep-treated anodes/cathodes is essential for fabricating uniform, well-dispersed electrodes with high capacity, thereby optimizing battery performance.

Advancements in X-ray photoelectron spectrometers have broadened their capabilities to effectively tackle these hurdles. X-ray photoelectron spectroscopy (XPS) emerges as an ideal method for scrutinizing the thin layers and interfaces of battery materials, due to its surface sensitivity (approximately 10nm) and ability to discern chemical states. Multi-technique XPS instruments offer an array of operational modes and analytical choices, facilitating comprehensive characterization of battery materials. This presentation showcases the utilization of a fully automated, multi-technique scanning XPS/HAXPES microprobe to address various challenges in battery material analysis. It incorporates an inert environment transfer vessel for air-free handling, a microprobe X-ray source with sub-5µm spatial resolution for precise area selection in small-area spectroscopic analysis and chemical mapping, and the utilization of hard X-ray and cluster ion gun sources for examining buried interfaces without compromising the underlying chemistry. The combination of these powerful capabilities allows for thorough analysis of battery materials at both macroscopic and microscopic levels, establishing a clear link between the chemistry and performance of electrodes treated with Engineered particles (Ep).

5:30pm AS-WeA-14 X-ray Photoelectron Spectroscopy for Battery Research Applications, Tatyana Bendikov, A. Maity, N. Yahalom, Y. Steinberg, H. Weissman, B. Rybtchinski, M. Leskes, Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS), as a surface sensitive technique with the sensitivity down to single atomic layer, provides unique

information about elemental composition and chemical and electronic states of elements in the material. It is not surprising that XPS is considered as one of the prominent tools in battery research, which enables determination of the electrodes/electrolyte composition during battery cycling, detection of the interfacial phases and follow their structural and compositional variations through depth profiling using ion sputtering. We show two examples where XPS was successfully used for the study of: 1) Sulfur-based composite carbon nanotube cathodes;¹ and 2) solid electrolyte interphase (SEI) on Na-Ion anodes.²

In spite of high reliability of the XPS technique and its assorted capabilities it should be taken into consideration that experimental conditions (high vacuum requirements) and X-ray radiation damage might alter the composition of the studied sample and can be mistakenly interpreted as non-existent battery reaction products. We present here systematic study of the LiTFSI, a widely used component of the nonaqueous battery electrolytes. We show how pumping conditions and/or prolonged X-ray exposure result in continuous deterioration of the LiTFSI. We also suggest partial solutions for deceleration of the decomposition processes during XPS measurements.

Literature:

1. N. Yahalom et. al, *ACS Appl. Energy Mater.* **2023**, 6, 4511–4519.
2. Y. Steinberg et. al, *manuscript in preparation.*

5:45pm AS-WeA-15 AVS Nellie Yeoh Whetten Awardee Talk: Investigating the Substrate Mediated Growth Pathways and High-Field Superconducting Behavior of Nb₃Sn Films for Particle Accelerator Cavities, Sarah Willson¹, University of Chicago; A. Harbick, Brigham Young University; R. Farber, University of Kansas; H. Lew-Kiedrowska, V. Do, University of Chicago; M. Transtrum, Brigham Young University; S. Sibener, University of Chicago

Niobium is the highest temperature elemental superconductor, making it the standard material for superconducting radiofrequency (SRF) cavities in next-generation linear accelerators. These facilities require cryogenic operating temperatures (< 4 K) to limit the formation of superconductivity-quenching hot spots in the near-surface region of the cavity. Widespread efforts are underway both to increase the accelerating fields and reduce the cryogenic burden by improving SRF surfaces. A promising solution is to coat the Nb SRF surface with a Nb₃Sn thin film *via* Sn vapor deposition. The higher critical temperature and critical field makes Nb₃Sn an ideal candidate for capping Nb surfaces. However, persistent Nb₃Sn material defects at the film surface, such as stoichiometric inhomogeneities and surface roughness, preferentially nucleate vortices under high fields that limit the accelerating performance of Nb₃Sn surfaces.

As part of a widespread interdisciplinary effort to optimize SRF accelerating capabilities, this work aims to develop a comprehensive growth model for pristine Nb₃Sn films. The complex interplay between the underlying Nb oxide morphology, Sn coverage, and Nb deposition temperature are examined by depositing Sn vapor on model Nb surfaces in an ultrahigh vacuum (UHV) environment with *in situ* surface characterization capabilities. Fundamental studies were scaled up to visualize how nanoscale features on the Nb oxide surface influence Sn and Nb₃Sn nucleation on unpolished polycrystalline Nb surfaces. These film growth studies collectively demonstrate that the Nb substrate defect sites are critical for stabilizing Sn adlayers.

Furthermore, the morphologies of stoichiometric defects on fully grown Nb₃Sn surfaces were investigated with computational support to simulate how the structures and sizes of Sn-poor and Sn-rich features influence the nucleation of vortices during SRF operation. Nb₃Sn films were prepared under varying conditions to demonstrate how the final cooldown steps of the vapor deposition process influence the stoichiometric homogeneity of the within the first 100 nanometers of the Nb₃Sn surface. Results indicate that the diameter and embedment of elemental Sn islands significantly alter the expected vortex nucleation field for a given global Sn composition. Understanding the effect of Nb₃Sn stoichiometric defect morphology on the high-field vortex nucleation is essential to systematically assess how different surface defects attenuate the achievable accelerating performance of Nb₃Sn coated cavities.

6:00pm AS-WeA-16 Silicon Wafer Doping with Mineral Films Prepared via Tethering by Aggregation and Growth, Peter Thissen, KIT, Germany

We investigate a new doping process of silicon wafers without making use of any highly toxic or corrosive chemical substances. Ultra-thin films of minerals, like hydroxyapatite (Ca₅(PO₄)₃OH), are prepared via tethering by

¹ AVS National Student Awardee

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aggregation and growth (T-BAG) and processed by rapid thermal annealing [1]. A variety of minerals can be used to effectively form metal silicates in contact with silicon oxide. This process is mainly thermodynamically driven and has already been well-studied using calcium silicate as an example [2]. One of the most thermodynamically stable calcium silicate phases is wollastonite (CaSiO_3). The main advantage of such formed phases is that they do not need to be etched with HF in the final step of the semiconductor processing; the direct use of mineral acids such as HCl or H_2S is sufficient to remove unwanted reaction byproducts. The doping method used, which uses the T-BAG technique for sample preparation, is not without inherent limitations. Although this method is widely used due to its simplicity and effectiveness, it is important to recognize its disadvantages, in particular the tendency towards an uneven distribution of the dopants across the semiconductor material. This phenomenon leads to an inhomogeneity across the sample, thus setting clear limits to the accuracy and reliability of the doping process. Consequently, although the T-BAG method is simple in sample preparation, its tendency towards non-uniform doping distribution highlights the need for careful consideration and possible refinement of future doping strategies. Using IR spectroscopy, we have already observed that the mineral decomposes at low temperatures (~ 500 K). The transport of 'P' through the native silicon oxide is driven by a phase transformation into a more stable thermal oxide [3]. At around 1000 K, diffusion of phosphorus into the region below the surface of the oxide-free silicon is observed. Finally, from our in-situ IR measurements in combination with electrical impedance spectroscopy, we conclude that phosphorus (a) is transported through the silicon oxide, (b) diffuses into the oxide-free silicon, and (c) finally changes the electrical activity of the silicon wafer.

[1] Vega, A.; Thissen, P.; Chabal, Y. J., Environment-Controlled Tethering by Aggregation and Growth of Phosphonic Acid Monolayers on Silicon Oxide. *Langmuir* 2012, 28, 8046-8051.

[2] Thissen, P., Exchange Reactions at Mineral Interfaces, *Langmuir* 2020 36 (35), 10293-10306.

[3] Longo, R. C.; Cho, K.; Hohmann, S.; Thissen, P., Mechanism of Phosphorus Transport through Silicon Oxide During Phosphonic Acid Monolayer Doping. *The Journal of Physical Chemistry C* 2018, 122, 10088-10095.

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