Atom Probe Tomography Focus Topic
Room: 230A - Session AP+AS+MC+MI+NS-MoM

Atom Probe Tomography of Nanomaterials
Moderator: Daniel Perea, Pacific Northwest National Laboratory

8:20am **AP+AS+MC+MI+NS-MoM1 Correlative Multi-scale Analysis of Nd-Fe-B Permanent Magnet**, ***Taisuke Sasaki***, *T. Ohkubo, K. Hono*, National Institute for Materials Science (NIMS), Japan **INVITED**

(Nd,Dy)–Fe–B based sintered magnets are currently used for traction motors and generators of (hybrid) electric vehicles because of their excellent combination of maximum energy product and coercivity. However, there is a strong demand to achieve high coercivity without using Dy due to its scarce natural resources and high cost. In Nd-Fe-B sintered magnets, thin Nd-rich grain boundary (GB) phase is a key microstructural feature affecting the coercivity. Although Nd-rich phases, e.g. Nd-rich oxides and metallic Nd, located at grain boundary triple junctions affect the formation of the Nd-enriched grain boundary phase during post-sinter annealing, their phase constitution, distribution and orientation relationships are still under debate.

This presentation will introduce examples of advanced characterization works to establish the global microstructural feature that controls the coercivity of Nd-Fe-B sintered magnets, e.g. the clarification of phase constitution and distribution of Nd-rich phases at the grain boundaries by correlative SEM and TEM characterization, and the identification of the structure and chemistry of thin Nd-rich grain boundary phases by high resolution HAADF-STEM and 3D atom probe. We found the coercivity decrease by carbon impurity can be explained by the decrease in the RE (RE: Rare earth) content in the thin Nd-rich grain boundary phase.

9:00am **AP+AS+MC+MI+NS-MoM3 Atom-Probe Tomography of Materials with Dimensions in the Nanometer Range**, ***Dieter Isheim***, Northwestern University **INVITED**

Nanometer-sized materials and particles seem to naturally lend themselves for investigation by atom-probe tomography (APT) which provides analytical imaging with subnanometer-scale spatial resolution in three dimensions. The material's characteristic dimensions may already be close to the one required to produce the electric field necessary for analysis by field-evaporation in an atom-probe tomograph and thus analysis seems straight forward. In practice, however, controlled manipulation and positioning of these nanoparticles or nanowires for APT analysis proves challenging since the support structure of an APT tip must be strong enough to resist the mechanical stresses exerted by the high electric fields involved. Additionally, the nanoparticles should ideally not be altered or damaged in the preparation process. These requirements can be met by modern processing techniques that combine suitable deposition methods for packaging nanoparticles in structures that are either ready for analysis, or suitable for subsequent APT tip preparation by a standard technique. Focused-ion-beam (FIB) microscopes equipped with a micro- or nanomanipulator and gas injection systems for electron- or ion-beam induced deposition provide a versatile platform for packaging, cutting, joining, and manipulating nanostructured materials, and thus to capture and target nanoparticles or specific microstructural features for APT analysis. This presentation explores these techniques to characterize a variety of nanometer sized and nanostructured materials, including nanodiamond particles and catalytically grown silicon nanowires.

9:40am **AP+AS+MC+MI+NS-MoM5 Exploring Atom Probe Tomography for Energy Storage and Conversion Materials**, ***Pritesh Parikh***, University of California, San Diego, *A. Devaraj,* Pacific Northwest National Laboratory, *S. Meng*, University of California, San Diego

The Sun forms the largest and most abundant source of energy on earth, yet it is not exploited to its full potential. Solar energy is a burgeoning field with a real chance to replace fossil fuels. The intermittent presence of sunlight can be mitigated by combining energy conversion devices such as solar panels with energy storage devices, namely Li ion batteries. A true solution is possible with the integration of both solar panels and batteries. With the general impetus towards adopting renewable sources for large scale energy storage and supply, fundamental studies on solar panels and batteries will provide new clues to design the next generation of energy devices. A Perovskite solar cell is one such technology that has the potential of high efficiency and low processing costs but a clear understanding of the role of different materials and their individual interactions is still lacking. The ability to identify and understand interfaces and multiple layers in a complex device such as solar cells and batteries is the need of the hour. Here we report on laser assisted atom probe tomography of energy storage and conversion devices to identify the spatial distribution of the elements comprising the various layers and materials. Recent progress and significant challenges for preparation and study of perovskite solar cells and battery materials using laser assisted atom probe tomography will be discussed. This opens up new avenues to understand complex mutli-layer systems at the atomic scale and provide a nanoscopic view into the intricate workings of energy materials.

10:00am **AP+AS+MC+MI+NS-MoM6 Atom Probe Tomography of Pt-based Nanoparticles**, ***Katja Eder***, *P.J. Felfer, J.M. Cairney*, The University of Sydney, Australia

Pt nanoparticles are commonly used as catalysts in fuel cells. There are a lot of factors which influence the activity of a catalyst, including the surface structure and geometry [1], d-band vacancy of the metal catalyst [2], the type of metal oxide support [3] and the oxidation state of the surface [4]. It is not yet fully understood in which way these factors influence the activity of the catalyst, since it is experimentally very difficult to get atomic scale information about the distribution of the atoms within such particle with conventional methods like transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunnelling microscopy (STM) and others. Models available which try to explain the structure-activity relationships therefore vary widely and there is much debate in the scientific literature about the underlying mechanisms of catalysis. For this reason it is crucial to conduct more research with methods that are able to obtain chemical information with a resolution on the atomic scale. In the past few years atom probe tomography (APT) has successfully been used in several studies to analyse nanoparticles [4-6]. APT provides a 3D reconstruction of the original specimen, which gives information about the chemical composition and the microstructure at a very high resolution. This method will enable us to have a closer look at the surface and interfaces as well as the composition of individual nanoparticles and solute atoms. In this talk we will present APT results of Pt nanoparticles, describing our efforts to prepare specimens with a reasonable yield and improved throughput compared to earlier studies, as well as some of the approaches used to overcome the difficulties that this challenge presents.

[1] A.R. Tao, S. Habas, P. Yang, Small, 4 (2008) 310-325.

[2] M.-K. Min, J. Cho, K. Cho, H. Kim, Electrochimica Acta, 45 (2000) 4211-4217.

[3] T. Akita, M. Kohyama, M. Haruta, Accounts of chemical research, (2013).

[4] T. Li, E.A. Marquis, P.A.J. Bagot, S.C. Tsang, G.D.W. Smith, Catalysis Today, 175 (2011) 552-557.

[5] Y. Xiang, V. Chitry, P. Liddicoat, P. Felfer, J. Cairney, S. Ringer, N. Kruse, Journal of the American Chemical Society, 135 (2013) 7114-7117.

[6] D.J. Larson, A.D. Giddings, Y. Wu, M.A. Verheijen, T.J. Prosa, F. Roozeboom, K.P. Rice, W.M.M. Kessels, B.P. Geiser, T.F. Kelly, Ultramicroscopy, (2015).

10:40am **AP+AS+MC+MI+NS-MoM8 APT & TEM Observations on Local Crystallization of NbO_2 used in Switching Devices**, *J.-H. Lee,* Pohang University of Science and Technology (POSTECH), Samsung Electronics, Republic of Korea, *J.-B. Seol,* ***C.-G Park***, Pohang University of Science and Technology (POSTECH), National Institute for Nanomaterials Technology (NINT), Republic of Korea **INVITED**

Threshold switching is the basis of electrical or thermal-driven phase change mechanism of oxide layer. That is, some oxide can change their conductivity from the level of insulators to that of metals with above certain current density. Although the mechanism responsible for threshold switching is not fully understood at present, it can be used as a switching device for the solution of sneak leakage problem. In order to apply the bipolar switching materials as the active layer of Resistive-switching Random Access Memory (RRAM), selection device which can minimize the sneak leakage current is needed. Among various candidates, we chose Nb-oxide for the selection device due to its superior compatibility with semiconductor structure. We have elucidated the mechanism of threshold switching of the amorphous NbO_2 layer by using in-situ transmission electron microscopy (TEM) technique combined with atom probe tomography (APT).

In this study, we proved that through an ex-situ experiment using TEM the threshold switching of amorphous NbO_2 accompanies local crystallization. The change in I-V characteristics after electroforming was examined by evaluating the concentration profile. APT combined with in-situ TEM probing technique was performed to understand the threshold switching in amorphous NbO_2. The local crystallization in amorphous NbO_2 was validated by the observed difference in time-of-flight (ToF) between amorphous and crystalline NbO_2. We concluded that the slower ToF of amorphous NbO_2 (a-NbO_2) compared to that of crystalline NbO2 (c-NbO_2) is due to the resistivity difference and trap-assisted recombination.

11:20am **AP+AS+MC+MI+NS-MoM10 Correlating Atom Probe Tomography with High-Resolution Scanning Transmission Electron Microscopy and Micro-Photoluminescence Spectroscopy: The Case of III-Nitride Heterostructures***,* ***Lorenzo Rigutti***, University of Rouen **INVITED**

Correlating two or more microscopy techniques on the same nanoscale object may yield a relevant amount of information, which could not be achieved by other means. In this contribution, we present several results of correlated studies of micro-photoluminescence (μ-PL), high-resolution scanning transmission electron microscopy (HR-STEM) and laser-assisted atom probe tomography (APT) on single nano-objects containing AlGaInN quantum well and quantum dot systems. We will show how this approach can be applied to the study of heterostructure interface definition, presence of defects, carrier localization and optical emission in III-N quantum confined systems [1]. Furthermore, we will show how the use of complementary techniques may be extremely helpful for a correct interpretation of atom probe results [2]. The possible implementation of micro-photoluminescence as an in-situ technique within the atom probe itself will finally be discussed [3].

[1] L. Rigutti et al., Nano letters (2014), 14, 107–114.

[2] L. Mancini et al. J. Phys. Chem. C (2014) 118, 24136-24151.

[3] L. Rigutti et al., Ultramicroscopy (2013), 132, 75-80.

Atom Probe Tomography Focus Topic
Room: 230A - Session AP+AS-MoA

Current and New Research Fields for Applications of Atom Probe Tomography
Moderator: Baishakhi Mazumder, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

2:20pm **AP+AS-MoA1 APT Studies of the Embrittlement of Fe-Cr Ferrite**, ***Mattias Thuvander***, Chalmers University of Technology, Sweden, *J. Odqvist, P. Hedström*, KTH Royal Institute of Technology, Sweden **INVITED**

Ferrite containing more than a few percent chromium is susceptible to embrittlement when subjected to elevated temperatures for sufficiently long periods of time. The phenomenon is often called '475°C embrittlement', indicating the temperature at which the effect is most rapid. The embrittlement is an issue for several important types of steel, including corrosion resistant ferritic steel, duplex stainless steel, cast austenitic steel and austenitic weldments, and limits their maximum service temperature (to about 300°C). The volume fraction of ferrite ranges from 100% in ferritic steel, to about 50% in duplex steel, down to 5-25% in austenitic castings and weldments (for which the presence of some ferrite is needed to avoid solidification cracking). The reason behind the embrittlement is the phase separation into two bcc-phases, Cr-rich α' and Fe-rich α, as can be seen in the binary Fe-Cr phase diagram. The phase separation results in an increase in strength and hardness but a decrease in ductility. Depending on Cr-content and temperature, the phase separation occurs by nucleation and growth (typically for low Cr contents) or by spinodal decomposition (typically for high Cr contents). Spinodal decomposition is an interesting phenomenon in physical metallurgy and it has been extensively studied for a long time. The phase separation occurs on the nanometer scale and during the early stages the concentration variations are subtle. Therefore, it is a challenging mechanism to study experimentally. Atom probe tomography (APT) is a well-suited technique, as small concentration variations on a small scale can be measured, also in the case when the phase separation has a complex 3D-structure, which is the case for spinodal decomposition. In this presentation, APT methodology for studying spinodal decomposition will be discussed. Also, results from several investigations concerning phase separation kinetics will be presented. For example, the influence of stress on spinodal decomposition in duplex steels, the influence of homogenization temperature on spinodal decomposition in binary Fe-Cr and the behavior of different ternary Fe-Cr-X systems will be addressed.

3:00pm **AP+AS-MoA3 Comparing APT Mass Spectral Ranging for Compositional Accuracy: A Case Study with Cast Duplex Stainless Steels**, ***Daniel Perea***, *A. Eaton, J. Liu,* Pacific Northwest National Laboratory, *S. Mburu, S. Schwarm, R. Kolli, S. Ankem*, University of Maryland

The mass spectrum of an atom probe tomographic analysis is a superposition of correlated mass-to-charge-state peaks and uncorrelated background counts. The compositional accuracy of a volume of material measured via atom probe tomographic analysis is dependent upon the manner in which the individual mass spectral peaks are ranged for integration. However, an accurate calculation of composition can be challenging due to a combination of complicated peak shapes, peak overlap, and background counts. Using data from both the α–ferrite and γ–austenite phases of a cast duplex stainless steel , we illustrate a methodology to account for the background counts, as well as to deconvolute overlapping peaks, in order to calculate composition that we compare to energy dispersive x-ray spectroscopy measurements.

3:20pm **AP+AS-MoA4 Chemical Imaging of Atmospheric Aerosols using Atom Probe Tomography and Multi-Modal Characterization**, ***Jia Liu***, *M.I. Nandasiri, L. Gordon, G. Kulkarni, V. Shutthanandan,* Pacific Northwest National Laboratory, *S.A. Thevuthasan,* Qatar Environment and Energy Research Institute, Qatar, *A. Devaraj*, Pacific Northwest National Laboratory

Global climate is significantly dictated by small particulates in the atmosphere known as aerosols. These atmospheric aerosol particles when subjected to certain humidity and temperature conditions can induce heterogeneous ice nucleation, which is directly sensitive to aerosol surface structure and chemistry. These ice nuclei are the precursors to snow fall and precipitation. Often natural atmospheric aerosols are found to be coated with sulfates and organic molecules. Elucidating the mechanism responsible for ice nucleation on coated or bare atmospheric aerosols requires understanding the structure, composition and chemical state of coated and bare aerosols. At EMSL we are developing a multimodal approach for imaging bare and coated aerosols utilizing a combination of atom probe tomography (APT), imaging X-ray photoelectron spectroscopy (XPS), focused ion beam scanning electron microscopy (FIB-SEM) and transmission electron microscopy (TEM). Imaging XPS provides the composition and chemical state of organic or inorganic elements within the top 5nm of the surface of aerosol particles with a spatial resolution of ~3 µm. FIB-SEM aids in understanding the morphology and porosity of particles both on the surface and sub-surface. TEM provides the atomic scale structural information and laser assisted APT provides sub-nanoscale compositional mapping of aerosols. TEM and APT are sub-single particle analysis techniques and can complement the individual aerosol particle measurements provided by the single particle laser ablation time of flight mass spectrometry (SPLAT). All these techniques provide specific multiscale chemical and structural information about the aerosol particles from the macro- to the atomic-scale. Specific examples from multimodal chemical imaging of mineral dust aerosols coated with varying concentration of sulfuric acid or organics will be presented along with the direct insights gained through this approach for improving ice nucleation parameterizations.

3:40pm **AP+AS-MoA5 Combining Atom Probe Tomography with TKD and FiB for Comprehensive Characterization of High Performance Materials**, ***Sophie Primig***, University of New South Wales, Australia, *K. Babinsky, P. Haslberger, C. Hofer, D. Lang, C. Turk*, Montanuniversität Leoben, Austria **INVITED**

Despite the increasing interest in atom probe tomography, this technique has so far almost exclusively been applied for chemical analyses of materials at the atomic scale. As nowadays the frontiers of material science are more and more being pushed towards the nanostructure, advanced comprehensive characterization techniques which provide both chemical and crystallographic information are required. For the crystallographic analysis of atom probe specimens several complementary techniques such as transmission electron microscopy have been applied that all have their advantages and drawbacks. Different approaches try to establish crystallographic information directly from the atom probe data itself which is still computationally challenging and not always possible. Another recently proposed straightforward way of quickly obtaining crystallographic information is the application of transmission Kikuchi diffraction on atom probe tips prior to the atom probe experiment. This procedure has so far only been successfully applied for positioning of grain boundaries close to the apex of the tips via focused ion beam milling.

The aim of the current study is to show applications of transmission Kikuchi diffraction on atom probe specimens of high performance materials and to demonstrate the strengths as well as the limits of these two complementary techniques. Four examples are shown which include boron segregation at prior austenite grain boundaries in a heat treatable steel, interlath retained austenite films with cementite in a bainitic steel, molybdenum carbides in a molybdenum alloy, and the preparation of grains with well-defined crystal directions in the tip axis of an iron-cobalt-molybdenum alloy.

4:20pm **AP+AS-MoA7 Atom Probe Tomography Studies of FeCo Nanocomposite Soft Magnetic Materials**, *A. Leary, V. Degeorge, V. Keylin,* Carnegie Mellon University, ***Arun Devaraj***, *J. Cui,* Pacific Northwest National Laboratory, *M. Mchenry*, Carnegie Mellon University

Nanocomposite soft magnetic materials exhibit high magnetization and low coercivity for application in power electronics, motors, and sensors. The composite nature of these materials, created by thermal annealing of rapidly solidified metallic glasses, offers many options to tune desired material properties. Grain sizes below ~30 nm are relevant to average the magnetocrystalline anisotropy between neighboring grains within an exchange volume. Chemical partitioning during devitrification creates variations in local composition compared to the nominal alloy composition. These variations impact material properties such as magnetostriction, Curie temperature, and grain size. Local composition measurements of annealed nanocomposites by Atom Probe Tomography link observed magnetic properties to the material structure. The impacts of chemical partitioning on diffusion limited grain growth, intergranular coupling at high temperature, and induced anisotropy are discussed.

Atom Probe Tomography Focus Topic
Room: 211D - Session AP+AS-TuM

New Applications of Atom Probe Tomography
Moderator: Arun Devaraj, Pacific Northwest National Laboratory

8:00am **AP+AS-TuM1 Development of Atom Probe Tomography for Studying Nuclear Corrosion Issues**, ***Daniel Schreiber***, Pacific Northwest National Laboratory **INVITED**

Material degradation and corrosion create significant challenges to nuclear energy production, both in terms of the structural integrity of plant components and also in the long-term disposal of high-level radioactive waste. For structural materials, stress corrosion cracking (SCC) continues to be a prominent issue for Ni-base alloys in the high temperature (~320 °C in pressurized water reactors) corrosive reactor environment. Despite decades of research, there has yet to be a consensus on the fundamental mechanisms that control SCC response. On the other hand, the long-term disposition of high-level nuclear waste generated by nuclear energy production continues to be an open question. Vitrification of high-level waste into a relatively stable form (e.g. borosilicate glass) is being actively pursued. However, disagreement exists about the long-term stability of the glass if/when exposed to ground water in a geologic repository due to an ill-defined rate-limiting process controlling glass dissolution. In both cases, high-resolution microscopy techniques including atom probe tomography (APT) provide unique opportunities to test various mechanistic theories with unprecedented spatial resolution and chemical sensitivity. Such studies have only recently been made possible through the advancement of site-specific focused ion beam (FIB) sample preparation methods and pulsed-laser APT systems, creating a unique environment for revolutionary discoveries.

In this talk, I will discuss the development of APT methods for characterizing SCC microstructures in select model and commercial alloys and also for characterizing the dissolution of model vitrified nuclear waste glasses. The corrosion of metals and the dissolution of glass present unique but overlapping challenges in sample preparation, data acquisition and data interpretation that will be discussed in detail. Highlights will be presented in both cases on how APT is changing the way we view the fundamental mechanisms dictating SCC of metals and glass alteration.

8:40am **AP+AS-TuM3 Using Aqueous Solutions by Cryo-Fixation As a Matrix for Analyzing Materials in APT**, ***Stephan Gerstl***, *B. Scherrer,* ETH Zürich, Switzerland, *J.M. Cairney,* University of Sydney, Australia, *R. Spolenak, R. Wepf*, ETH Zürich, Switzerland **INVITED**

Atom probe tomography has progressively engaged the world of materials characterization with 3-dimensional nanometer-level maps of various dense materials. These atom maps have been the attraction of the technique because they enable new perspectives and analysis of solid materials literally atom by atom. The analysis of soft organic materials, even aqueous solutions, has however been a long-standing issue as it is impaired by contamination, uncertain phase formation, and questionable observed states. These outcomes have been interrogated, retested, and re-analyzed to better understand the artifacts involved. Here we present the development steps achieved together with the APT results obtained of three aqueous based solutions: a water-based citrate solution, a 1:1 water-ethanol mixture, and a commercially available marginally alcoholic beverage. These aqueous solutions were chosen so as to exhibit differences in their mass-spectrum response due to their dissimilarities. The methodologies enabling these analyses require arresting the liquids so they are stable in vacuum environments, sharpening them to a needle geometry, and transporting them between chambers whilst not altering their structural integrity; all steps being done close to LN_2 temperatures. The main challenge was with contamination, which needs to be minimized and separated from the material of interest in the analysis. The cryo-fixation method involves plunge freezing the region of interest (ROI) in cryogenic liquids, sharpening the ROI in a FIB fitted with a cryogenically cooled stage, and field evaporating it in a retrofitted cryo-transfer enabled LEAP 4000X-HR.

All aqueous specimens could be analyzed successfully; with the resulting amounts of ROI analyzed being small (only a thin film is probed due to sample geometry), trends and fluctuations in ion concentrations have been interrogated and will be presented.

The application space of this technique will be considered in terms of using fluids as matrices and designing the experiments to increase the volume of soft materials analyzed.

11:00am **AP+AS-TuM10 Atom Probe Tomography Investigation of TiSiN Thin Films Made Possible by ^{15}N Isotopic Substitution**, ***David Engberg***, Linköping University, Sweden, *L.J.S. Johnson,* Sandvik Coromant, Sweden, *M.P. Johansson-Jöesaar,* SECO Tools AB, Sweden, *M. Odén,* Linköping University, Sweden, *M. Thuvander,* Chalmers University of Technology, Sweden, *L. Hultman*, Linköping University, Sweden

TiSiN is one of the most important materials for commercial wear resistant coatings on cutting tools. Understanding of the growth and structure of these coatings has become increasingly important for optimizing their performance. Yet knowledge regarding the solid solubility, distribution, and stoichiometry of SiN_y has been lacking in the complex metastable TiN-SiN structure. Atom probe tomography (APT) in combination with analytical electron microscopy provides a way to attain compositional information in 3D on the nanometer scale. However, mass spectrum overlaps of N and Si ions have so far prevented such APT analyses. By growing TiSiN coatings with ^{15}N using cathodic arc deposition, we show that the mass spectrum overlaps of Si and N can be largely avoided. $TiSi^{15}N$ films of two compositions, $Ti_{0.81}Si_{0.19}{}^{15}N$ and $Ti_{0.92}Si_{0.08}{}^{15}N$ in a predominantly cubic structure, have been studied using APT. We find evidence of Si-Si clustering on the nanometer scale, while there are no indications of overstoichiometric SiN_y ($y \approx 1$).

11:20am **AP+AS-TuM11 Investigating the Alternating Cation/Anion Compositions in a High-Voltage Li-Mn-Rich Oxide Electrode during First Charge-Discharge Cycle using Atom Probe tomography**, ***Baishakhi Mazumder***, *D. Mohanty, C. Daniel, D. Wood III*, Oak Ridge National Laboratory

High-voltage layered lithium and manganese-rich (LMR) oxides are potential cathodes for high-energy-density lithium-ion batteries for electric vehicles1. Unfortunately, structural transformation during charging and discharging in these oxides2 leads to undesired phenomena, such as voltage fade during subsequent cycles and lower columbic efficiency in the first cycle, that remain stumbling blocks for practical usage. Understanding the micro-structural changes during the first cycle is critical to obtaining fundamental insight regarding the activation mechanism(s) related to the first cycle capacity loss. In this work, Atom Probe Tomography (APT) has been employed to obtain the 3D microstructural and sub-nm-level compositional information of LMR oxides during the first cycle to resolve the activation mechanism(s) that lead to structural transformation.

The greatest challenge for APT analysis from the actual electrode materials is the complexity in creating needle-shaped specimens. Owing to the discontinuous geometry of the electrode, which is characterized by non-uniform interconnected channels, it is extremely difficult to make a structurally stable needle for controlled field evaporation. Micro-fractures and irregular evaporation due to differences in evaporation fields between the composite elements during APT analysis is also challenging. Additionally, experimental parameters, including tip temperature, laser energy, and detection rate, all strongly impact the field-evaporation and subsequent data analysis. By overcoming these challenges, reliable and reproducible data has been obtained after optimizing the experimental parameters and developing a reliable procedure to prepare stable samples. Mass spectra reveal molecular complexes MxOy for M=Ni,Mn,Co, while the Li appears predominantly as elemental ions. The 3D distributions as well as the compositions of each element were obtained for each sample at different states of charge during the first cycle. These data provides insight towards understanding the structural rearrangements during the first charge-discharge cycle that correlates with the first cycle irreversible capacity loss.

1) M.M. Thackeray, et al., J. Mat. Chem.17 3112 (2007)

2) D. Mohanty, et al., Chem. Mat. 26 6272 (2014)

Research supported by CNMS, which is a DOE Office of Science User Facility.LMR material was obtained from Argonne National Laboratory. The electrodes/cell fabrication, and cell testing were carried out at the DOE's Battery Manufacturing R&D Facility at Oak Ridge National Laboratory, which is supported by VTO within the core funding of the ABR subprogram. Authors thank Dr. Jianlin Li at ORNL for fabricating electrodes.

Plasma Science and Technology
Room: 210B - Session PS+AP+SE-ThA

Advanced Ion Implantation and Plasma Doping
Moderator: Aseem K. Srivastava, Applied Materials, Inc.

2:20pm **PS+AP+SE-ThA1 Evolutionary Trends in Ion Implantation**, ***Anthony Renau***, Applied Materials, Varian Semiconductor Equipment **INVITED**

Since the 1960s and 1970s ion implantation has been used for the p- and n-type doping of semiconductors. The ability of ion implantation to abruptly alter the stoichiometry of the substrate has made it a very attractive technology for making transistors with the required drive characteristics, by accuratley manipulating dopant concentrations in the contact and channel regions. It is used to control carrier density, channel length, contact resistance, isolation and other key device attributes.

There have been significant enhancements to enable ion implant to continue to meet semiconductor doping needs. These include the development of ribbon ion beams, substrate temperature control, accurate beam angle control and novel methods for precisely varying the dose over the substrate. These improvements have also enabled the technology to be used for a rapidly growing number of non-doping applications.

Today, the majority of implants are done not for doping, but are instead used for some form of materials modification or engineering. These include, for example, strain control, pre- or post-treatments to improve some other process step, and lattice enginering for isolation or diffusion control.

In this paper we will discuss some of the improvements to the technology and the applications that have benifited from these. We will also describe how directed ribbon beam technology, similar to that used for implanters, can also be used to improve materials engineering applications as diverse as etch and CMP.

3:00pm **PS+AP+SE-ThA3 Conformal Arsenic Doping using a Radial Line Slot Antenna Microwave Plasma Source**, ***Hirokazu Ueda***, Tokyo Electron Limited, Japan, *P. Ventzek,* Tokyo Electron America, Inc., *M. Oka, Y. Kobayashi, Y. Sugimoto,* Tokyo Electron Ltd., *T. Nozawa,* Tokyo Electron Ltd., Japan, *S. Kawakami*, Tokyo Electron Ltd. **INVITED**

Doping and activation of non-planar topographic structures is important for the fabrication of functional FinFET and nanowire based devices to name a few. Conformal plasma arsenic doping of topographic (fin) structures was achieved using RLSA^{TM} microwave plasmas with low temperature annealing. To show that the arsenic concentrations were identical at the fin top and sides, dopant concentrations were measured precisely by TEM and SEM EDX for both plasma doping and subsequent annealing steps. We found that doping using plasmas generated by lower RF bias operation coincident with high microwave power was key to obtaining perfectly conformal arsenic dose/profiles after annealing. The RLSA^{TM} microwave plasma facilitates high enough electron density at the plasma generation region to supply enough reactive dopants for sufficient dose. The high plasma density plasma allows for operation in a low RF power and high process pressure regime. This regime yields ions with sufficient flux and energy for dopant integration into and redistribution around the topographic structure. At the same time low enough energy ions can be controllably accessed to ensure fin damage is eliminated. We also demonstrate optimized rf bias power of the microwave RLSA^{TM} plasma enables additional control of dopant conformality post SPM wet cleaning step. The wet clean poses a significant challenge for dose retention as cleans tend to remove oxidized or otherwise disordered silicon material. The source of dose retention is shown to be related to dopant transport through a ternary (As-Si-O) oxide layer, segregation effects and the stable nature of the oxide. The presentation will include experimental and computational results related to dose conformality and retention. Comments related to the future of plasma doping technology including advanced materials, metrology and control will round out the presentation.

4:00pm **PS+AP+SE-ThA6 Practical Application of Atom Probe to Analysis of Ion Implantation**, ***Ty Prosa***, CAMECA Instruments Inc. **INVITED**

Characterization of implanted dopants and impurity atoms within individual silicon nano-devices is critical to the semiconductor industry. While secondary ion mass spectrometry (SIMS) depth profiles achieve a high level of quantification with ion implanted standards in various matrices, atom probe tomography (APT) offers a unique combination of high analytical sensitivity coupled with high spatial resolution [1]. SIMS achieves its sensitivity by analyzing relatively unconstrained sample volumes, analyzed areas often greater than several hundred square microns. Square microns of material cannot be analyzed by APT and so it can never compete with SIMS for sensitivity at the micron scale; however, the situation is very different at the nanoscale—the regime of individual device volumes. Within this regime APT has high, uniform, quantitative chemical sensitivity with sub-nanometer spatial sensitivity.

Understanding the precision and accuracy of APT when applied to ion implanted dopant profiles is essential for general adoption by the semiconductor industry. Three-dimensional atom positions are determined using a simple point-projection methodology [2]. Adopting best practices within the constraints of this methodology is necessary to allow uniform and unbiased determination of atom positions and depth profiles. Although the ultimate sensitivity of APT is determined by counting statistics, it is well known that counting statistics alone do not fully account for accuracy limitations. The free parameters available within the reconstruction process are often dominant in terms of total observed error.

During this presentation, a number of examples will be shown of APT applied to the analysis of dopant distributions in relevant structures. The focus will be ion implanted structures with discussion of best practice approaches to minimize error and remove bias by the practitioner. Material structures include a series of NIST Standard Reference Material implants into silicon [3] and additional implants into GaN-based materials.

[1] T.F. Kelly and D.J. Larson, *Annual Reviews of Materials Research* 42 (2012) 1.

[2] P. Bas et al., *Surf. Sci.* 87/88 (1995) 298.

[3] R.R. Greenberg et al., *Radioanal. Nucl. Chem,* 245 (2000) 57.

4:40pm **PS+AP+SE-ThA8 Optical Emission Spectroscopy to Determine Plasma Parameters in an Oxygen Inductively Coupled Plasma**, ***Nathaniel Ly***, *J. Boffard, C.C. Lin, A.E. Wendt,* University of Wisconsin - Madison, *S. Radovanov, H. Persing, A. Likhanskii*, Applied Materials, Inc.

The success of ion implantation to precisely modify substrate properties requires control of the incident ion energies to achieve the desired depth of the implanted ions. Oxygen plasmas generally contain both O^+ and O_2^+ positive ions, and in plasma immersion ion implantation (PIII) of oxygen, the two will produce different concentration depth profiles due to their different energy/mass ratios. Predicting the overall profile thus requires knowledge of the relative fluxes of the two ion species. Motivated by the long term goal of a robust predictive model, here we combine experiment and numerical simulation to investigate the feasibility of using non-invasive optical emission spectroscopy (OES) to monitor plasma parameters in an oxygen inductively-coupled plasma. Initial experiments made use of a small admixture of argon with the oxygen to take advantage of established techniques involving argon OES. In addition to recording argon emissions, measurements of multiple O, O_2, O^+, and O_2^+ emission intensities were made as a function of pressure (1-30 mTorr) and power (500-2000 W). An emission model makes use of available electron impact excitation cross sections for argon and atomic and molecular oxygen to relate measured emission spectra to corresponding plasma parameters, including electron temperature and the dissociation fraction of the neutral oxygen. Data taken while as a function of the percentage of argon in the Ar/O_2 mixture showed that even a very small admixture of argon significantly affected the oxygen plasma properties, and more recent experiments have thus focused on oxygen OES in a pure oxygen plasma. The CRTRS 2D/3D plasma code self-consistently and semi-implicitly solves for ICP power deposition and uses Poisson's equation to solve for the electrostatic potential and dynamics of electrons and ions in the drift-diffusion approximation (or full momentum equations). The code also solves for the electron temperature, and generation and quenching of excited states as well as their dynamics. The experimental results are used in combination with simulation predictions to understand the dependence of plasma parameters, including the relative fluxes of O^+ and O_2^+, on the operating parameters.

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5:00pm **PS+AP+SE-ThA9 Adhesion Improvement of Carbon Nitride Coatings on Steel Surfaces by Metal Ion Implantation using HiPIMS**, ***Konstantinos Bakoglidis***, *G. Greczynski, S. Schmidt, L. Hultman*, Linkoping University, Sweden

Carbon based thin films are materials with low friction and wear resistance. Deposition of C based thin films as coatings on steel substrates can enhance the tribological performance of steel surfaces. Adhesion of magnetron sputtered C based coatings on steel substrates is, however, often insufficient, leading to film delamination or flaking after the deposition. Adhesion is essential when such films are exploited in tribological applications and can be improved by using ion etching of the steel surface prior to film deposition. Several ion etching techniques are used, among them metal ion etching, for ion implantation in order to prepare the steel surface for the C film deposition. Moreover, high power impulse magnetron sputtering (HiPIMS) offers high metal ionization conditions and effectively enhances ion implantation into the steel subsurface. In this study, we used four different metal targets, namely Al, Cr, Zr, W, in HiPIMS mode in Ar-based plasma with a pressure of 200 mPa, and under a negative applied bias voltage of 900 V, which was synchronized with the cathode pulse. All targets were operated with an energy per pulse of 15 J, with pulse width of 200 µs, an etching time of 30 s, while the frequency was set at 100 Hz. A carbon nitride (CN_x) thin film was deposited after each etching step, using a graphite target in DC mode, operated at 1400 W, in a N_2/Ar gas mixture with a ratio of 0.16, and at a temperature of 150 °C, while the pressure was kept constant at 400 mPa. In all cases except Zr, a thin metal interlayer was obtained, with thicknesses < 20 nm, while adhesion of CN_x films on steel surface was dramatically improved when W ions were used for the pre-treatment phase.

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