Atom Probe Tomography Focus Topic
Room: 203 A - Session AP+AS+SS-TuA

Microstructural and Interface Analysis of Metals Subjected to Various Conditions
Moderator: A. Devaraj, Pacific Northwest National Laboratory

2:00pm **AP+AS+SS-TuA1 Multivariate Analysis of Atom Probe Tomography Data: Methods to Simplify Factor Interpretation**, ***M.R. Keenan***, Consultant, *V. Smentkowski*, General Electric Global Research Center

Multivariate statistical analysis has been used successfully for several years to analyze spectral images acquired in three spatial dimensions. Examples include energy dispersive x-ray images obtained from serially sectioned samples, and depth profiles in ToF-SIMS. More recently, multivariate methods have begun to be applied to atom probe tomography (APT) data. The analysis of APT data, however, poses some unique challenges, and it is important for the APT community to understand the principles that underpin the multivariate approach in order to maximize its effectiveness. The basic assumption made during multivariate analysis is that the composition of a sample at a particular location can be described as a linear combination of a limited number of “pure components”, with each component having a characteristic spectral signature. The job of multivariate analysis, then, is to discover the number components, extract spectral information suitable for identifying them, and determine the spatial distributions of their abundances. The primary tool of multivariate analysis is the Singular Value Decomposition (SVD), or the closely related Principal Component Analysis (PCA). These techniques distill the chemically relevant information in high-dimensional raw data sets into a small number of factors or components. These components, however, are abstract and not easily interpreted. For instance, typical components may contain negative spectral features and abundances, which are not physically plausible. In order to find a more straightforward representation of the components, they can be post-processed to impose certain constraints or preferences on the factor model. In this talk, a chemically simple sample will be used to illustrate some of these multivariate concepts in geometric terms. In particular, factor rotation procedures, such as the Varimax rotation, will be shown suitable for obtaining factor models that are in some sense simple, either spectrally or spatially, and the natural duality of the spectral and spatial domains will be highlighted. Multivariate Curve Resolution (MCR) will also be considered. MCR imposes constraints, often non-negativity, on the model components. MCR is problematic, however, in the presence of high noise levels typical of APT data, and some approaches for improving the fidelity of MCR models will be presented. APT is capable of producing quantitative results. As will be shown, achieving them with multivariate analysis requires tailoring the methods to the specifics of APT and paying careful attention to the details.

2:40pm **AP+AS+SS-TuA3 The *Renaissance* in Metallurgical Design and the Role of Atom Probe Microscopy**, ***S.P. Ringer***, The University of Sydney, Australia **INVITED**

The design of materials that demonstrate properties that are ordinarily in conflict with each other is a tantalising frontier of materials science and engineering. The design of metallic (not glassy!) aluminium alloys and new 3rd generation steels with remarkable combinations of high strength and ductility[1], magnetic carbon with a tuneable bandgap[2], and materials that exhibit magnetism and superconductivity in the same phase[3] represent examples of new metals and materials that exhibit highly sought after properties that are usually in conflict with each other. In these cases, our approach to overcoming these property conflicts is via atomic clustering within the solid solution, and that is the topic of this presentation.

In fact, short-range ordering, atomic clustering, segregation and site-occupancy exert a major influence on the phase transformation pathways, and transformation kinetics in many technologically important supersaturated solid solutions. So, how can these non-periodic structures be described, measured and, ultimately, ‘designed’.

I will discuss a new theory for short-range order[4,5] that provides a framework for describing the atomistic configurations in *n*-component solid solutions. The characterisation of such materials will then be discussed, in detail. The challenging issues associated with scattering based approaches using X-rays, neutrons or electrons, will be set out and it will be shown that there exist complex convolutions in the diffracted intensity that make the measurement of this 3D atomic architecture extremely challenging.

Finally, I will discuss our approach to addressing these issues using atom probe microscopy. We have recently modelled the origins of resolution in the atom probe, computed advanced spatial distribution maps, which are analogous to Patterson functions in scattering experiments, and used these new tools to devise an approach for ‘lattice rectification’, analogous to aberration correction in TEM. These techniques[6] are revealing a rich and complex hierarchical architecture of atomic structures within solid solutions, and at microstructural interfaces and these are all discussed in terms of the renaissance in metallurgical design that we in the midst of.

[1] Liddicoat, Liao, Zhao, Zhu, Murashkin, Lavernia, Valiev and Ringer, “Nanostructural hierarchy increases strength of aluminium alloys”, *Nature Communications*, Vol. 1, Article 63 (2010).

[2] Cui, Zheng, Liu, Li, Delley, Stampfl and Ringer, “Magic numbers of nanoholes in graphene: tunable magnetism and semiconductivity,” *Physical Review B*, Vol. 84, Article 125410 (2011).

[3] Yeoh, Gault, Cui, Zhu, Moody, Li, Zheng, Li, Wang, Dou, Sun, Lin and Ringer, “Direct observation of local potassium variation and its correlation to electronic inhomogeneity in $(Ba_{1-x}K_x)Fe_2As_2$ pnictide”, *Physical Review Letters*, Vol. 106, Article 247002 (2011).

[4] Ceguerra, Powles, Petersen, Marceau, Moody and Ringer, Short-range ordering in multicomponent materials, *Acta Crystallographica A*, (2012, in press)

[5] Ceguerra, Powles, Moody and Ringer, “Quantitative description of atomic architecture in solid solutions: a generalized theory for multicomponent short-range order”, *Physical Review B*, Vol. 82, Article 132201 (2010).

[6], Gault, Moody, Cairney and Ringer, “*Atom probe microscopy*”, Springer – monograph series in materials science , (2012).

4:40pm **AP+AS+SS-TuA9 Atom Probe Tomography Investigations of Surface and Grain Boundary Oxidation in Ni-Cr Alloys Exposed to High-Temperature Water**, ***D.K. Schreiber***, *M.J. Olszta, S.M. Bruemmer*, Pacific Northwest National Laboratory

Ni-base, Cr-containing alloys have been selected for use as structural components in many aggressive environments because of their well-known corrosion resistance. In most oxidizing environments, the high Cr content of these alloys results in the formation of a protective Cr-rich oxide film. However, Ni-Cr alloys have been shown to be susceptible to localized corrosion in high-temperature hydrogenated water environments as found in the primary system of pressurized water reactors. Mechanisms controlling this degradation are being investigated using high-resolution analytical electron microscopy and atom probe tomography. Examples will be presented from Ni-Cr model binary alloys (5-30Cr), commercial alloy 600 (Ni-17Cr-9Fe) and alloy 690 (Ni-30Cr-9Fe) samples. In all cases, grain boundaries are found to play a significant but varied role in the observed corrosion behavior. In lower Cr alloys (5-20%), the grain boundaries are preferentially attacked and exhibit extensive oxidation to a much greater depth than the surrounding matrix. In sharp contrast, alloys with 30% Cr form a continuous layer of Cr_2O_3 directly above grain boundaries that protects the grain boundary from oxidation. Localized filamentary oxidation is observed into the metal matrix away from the intersection of the grain boundary with the surface where a continuous layer of Cr_2O_3 does not form.

5:00pm **AP+AS+SS-TuA10 Space Charge Effects in Atom Probe tomography**, ***I. Blum***, *F. Vurpillot, L. Rigutti, A. Gaillard, D. Shinde, J. Houard, A. Vella, B. Deconihout*, Groupe de Physique des Matériaux, France

Because of the relatively low ion currents observed during an APT analysis (0.1 to 0.0001 atom/pulse), it is generally assumed that the evaporated ions do not interact with each other during the field evaporation of the sample. It was shown recently, however, that ion-ion interactions do occur after dissociation of molecular ions [1], which can be observed during the analysis of compound semiconductors [1-2]. Indeed, coulomb repulsion between the dissociation products modifies their trajectory in a manner similar to space charge effects in high intensity beams of charged particles.

In this work, we combine the information on the time-of-flight and impact positions on the detector of multiple events to study this phenomenon. Experimental results on GaN and ZnO samples are explained by taking into account the orientation of the molecule during dissociation, the shape of the electric field around the tip and the dissociation potential. We show that the coulomb repulsion between the dissociation products occurs in a direction of space that depends on the orientation of the molecule during dissociation. Therefore, the coulomb interactions can have a significant effect on their impact positions on the detector but can also have an effect on the time-of-flight of the particles. The times-of-flight and impact positions of the dissociation products are correlated and contain potential information about the physics of the dissociation of the original molecule in high electric field. These results are compared to simple simulations of the ions trajectories in the electric field. We also discuss the potential effect of this phenomenon on the quality of APT data and provide simple methods for its identification.

[1] M. Müller, B. Gault, G. D. W. Smith, and C. R. M. Grovenor, "Accuracy of pulsed laser atom probe tomography for compound semiconductor analysis," *Journal of Physics: Conference Series*, vol. 326, p. 012031, Nov. 2011.

[2] D. W. Saxey, "Correlated ion analysis and the interpretation of atom probe mass spectra.," *Ultramicroscopy*, vol. 111, no. 6, pp. 473–479, May 2011.

5:20pm **AP+AS+SS-TuA11 Atom Probe Analysis and Challenges to Study a High-k Dielectric Grown on GaN**, ***B. Mazumder**, X. Liu, F. Wu, U.K. Mishra, J.S. Speck*, University of California, Santa Barbara

Al_2O_3 has emerged as an appropriate gate dielectric for III-nitride based electronic devices. Major growth challenges for such high-k/GaN interfaces include unwanted GaN oxidation, impurity etc during deposition may result in the formation of electrically active defects. In addition to prior structural investigations of such systems, the relation between atomic structure, chemistry and electrical properties of these interfaces is poorly understood. Atom probe tomography (APT) was used to determine structural information related to interface abruptness, layer composition including impurity content. It is quite challenging to analyze dielectric/insulating oxides multilayers using atom probe. Micro fractures, irregular evaporation etc due to the evaporation field difference between the layers can make the analysis challenging. Additionally, experimental parameters including tip temperatures, laser energy, and detection rate all strongly impact the field evaporation and subsequent data analysis. In this study we have reported reliable and reproducible data with high measurement yield by optimizing experimental parameters and using a suitable capping layer.

Ga-face ((0001) c-plane) GaN samples were grown by metal organic chemical vapor deposition (MOCVD). Al_2O_3 layers were grown on GaN, both by MOCVD and atomic layer deposition (ALD) system for a comparative study . These samples were then analyzed in Local Electrode Atom Probe 3000X HR. The experimental parameters were optimized for the oxide/semiconductor system. Initially the measurement yield was very low with a metal cap layer (Ni, Cr). Replacing it by a low temperature GaN cap layer the measurement yield was increased substantially. Thorough compositional analysis and roughness measurements were done and it was found that the interface is relatively rough and not atomically abrupt. However no presence of Ga_xO_y was found in both the cases. Qualitative estimation of carbon impurities within dielectric was done for both the samples and was found to be in the order of $10^{19}/cm^3$, however the MOCVD sample shows higher carbon concentration than those grown by ALD. From the C-V measurements the volume trap charge density was estimated to be around 2 $x10^{19}$ $cm^{-3}$and 3.9 $x10^{19}$ cm^{-3} for ALD and MOCVD samples respectively, those are of the same order as the carbon concentration determined from the atom probe measurements. By varying the growth temperature the amount of C impurity was controlled. In conclusion, atom probe was successfully used to investigate the dielectric/III-V system in depth, which provides valuable feedback for growth optimization required for better device fabrication.

5:40pm **AP+AS+SS-TuA12 A Correlated Micro-Photoluminescence, Scanning Transmission Electron Microscopy and Atom Probe Tomography Experiment on the Same Nano-Object Containing a Set of InGaN/GaN Multi-Quantum Wells**, ***L. Rigutti**, I. Blum, D. Shinde, D. Hernandez Maldonado, W. Lefebvre, J. Houard, A. Vella, F. Vurpillot,* Groupe de Physique des Matériaux, France*, M. Tchernycheva,* Institut d'Electronique Fondamentale, France*, C. Durand, J. Eymery,* CEA/CNRS/Université Joseph Fourier, France*, **B. Deconihout***, Groupe de Physique des Matériaux, France

In this contribution, we present a correlated experiment on a single nanoscale object containing a set of InGaN/GaN non-polar multiple-quantum wells. The nano-object has been analyzed by micro-photoluminescence spectroscopy (µPL), high-resolution scanning transmission electron microscopy (HR-STEM) and atom probe tomography (APT). The observed µPL narrow emission lines, polarized perpendicularly to the crystal c-axis and with energy in the interval 2.9 eV – 3.3 eV. The STEM data allow concluding that the optical polarization is related to the crystallography through the selection rules for the lowest-energy excitonic transition in the wurtzite structure. STEM also constitutes an important reference for the 3D atom probe reconstruction of this large (16 QWs) multi-quantum well system. Atom probe data evidence that the In distribution inthe wells is not regular, and that In-rich regions, with InN fraction up to 20%, form patterns propagating from one well to the other. All these observations coherently support the interpretation that the optical emission lines observed in µPL are related to exciton states localized in potential minima induced by the irregular 3D In distribution within the QW planes. This novel correlative technique can be in principle applied to a wide class of quantum confining emitters and nano-objects, and is susceptible to be implemented as a coupled *in situ* technique within the atom probe itself.

Atom Probe Tomography Focus Topic
Room: Hall B - Session AP-TuP

Atom Probe Tomography Poster Session

AP-TuP1 Atom Probe Tomography of Energy and Environmental Materials, ***D.E. Perea**, A. Devaraj, R.J. Colby, J. Liu, D.K. Schreiber, J.E. Evans, S.A. Thevuthasan*, Pacific Northwest National Laboratory

Buried interfaces and surfaces play an essential role in the function of many materials for energy, environmental, and biological applications. An understanding of the physics and ultimate the ability to engineer materials with specific properties is aided by an atomic level understanding of the composition and morphology of interfaces. Atom probe tomography (APT) is a 3-dimensional compositional mapping technique based on the field evaporation of individual atoms from the tip of a needle-shaped specimen. At the Environmental Molecular Sciences Laboratory (EMSL), we are pushing the limits of APT analysis to study a wide variety of energy and environmental materials. We will present several examples that exemplify the breadth of materials which include semiconductor nanowires for high performance solar cell and transistors, geologic minerals used for atmospheric carbon sequestration, and glass materials for the vitrification of controlled waste.

AP-TuP2 Advantage of NbTiN over NbN in Superconducting Properties of Ultra-thin Films, ***M. Guziewicz**, A. Laszcz, J.Z. Domagala, K. Golaszewska, A. Czerwinski, W. Slysz*, Institute of Electron Technology, Poland

Progress in quality of ultra-thin superconducting niobium nitride films for fabrication technology of Superconducting Single Photon Detectors is still observed. Photon detection bases on a recording of current collapse pulse caused by a photon absorbed in the nanostructure film . Materials proved to be effective are Nb-nitride layers and the layers containing Ti . The latter applied in the detector structure have the advantage in the quantum efficiency and reduced noise by one decade compared to the NbN film . So far, there are no known causes of advantages of this material, but can be traced to them in a better quality of structure and uniformity of composition, which reduces the probability of scattering electron pairs on superconductors current defects . The confirmation of these assumptions may be the observation that better parameters are characterized by the detectors made with layers of amorphous than polycrystalline NbN and compete well with epitaxial NbN layers of single crystal characteristics . It can be find some papers where influence of substrate, sputtering deposition parameters and film thickness of NbN or NbTiN on critical temperature were studied. Our niobium nitrides films deposited on (0001)Al_2O_3 reveal excellent both superconducting and structure properties. Extensive characterization of the films using XRD, high resolution TEM and AFM were performed. High epitaxial quality of NbN and NbTiN films grown on the Al_2O_3 substrates is proved by HRXRD and HRTEM studies. The results of the studies on both NbN and NbTiN films reveal one cubic phase with NaCl-type structure. The critical temperatures of NbN and NbTiN films with thickness of few nm grown on the Al_2O_3 substrates are in range 4K ÷ 7K, but post-grown annealing of the films at 1000^{o}C in Ar increases temperature up to 12K or above. Moreover, the 5 nm thick NbTiN film deposited on sapphire at optimized conditions and annealed discloses the best superconducting properties - critical temperature of 14 K as well as extremely high critical current density of 12·MA/cm^2, while the critical current density of 3 MA/cm^2 was attained for the NbN film. This is the highest value measured on so thin Nb-nitrides films. The improvement in superconductor parameters can be explained due to reduced strain and defects by high temperature annealing of the film. Rocking Curve of the 111 Bragg reflection on the NbTiN is extremely narrow, ≈10 arcsec, characterising the best single crystals. Higher critical current density is almost certainly attained due to lower atomic concentration of oxygen contamination in the NbTiN films than in the NbN films.

Atom Probe Tomography Focus Topic
Room: 203 A - Session AP+AS+EM+MI+TF-WeM

APT Analysis of Semiconductor, Magnetic, and Oxide Materials
Moderator: T. Li, University of Sydney, Australia

8:00am **AP+AS+EM+MI+TF-WeM1 Progress in Planar-Feature Spatial Reconstruction for Atom Probe Tomography**, ***D.J. Larson**, B.P. Geiser, T.J. Prosa, T.F. Kelly*, CAMECA

In the last decade, the applicability of atom probe tomography (APT) has undergone a revolution [1] due to: 1) improved specimen preparation due to focused ion beam milling, 2) improved field of view due to the advent of a local electrode or other ion optical methods, and 3) reinvention of the use of lasers to induce field evaporation. This combination has created challenges in the area of spatial data reconstruction algorithms for APT for two reasons. Firstly, datasets collected at wider field of view are not accurately reconstructed using small angle approximation algorithms. Secondly, heterogeneous specimens containing multiple phases are more likely to yield, which creates challenges in reconstruction due to the non-hemispherical specimen shapes arising from field evaporation.

The most common algorithm for APT data reconstruction has been used with minimal changes for nearly twenty years [2] and has two main limitations: 1) the field evaporated surface is reconstructed as a hemispherical shape and 2) the atomic volume/depth increment is independent of X or Y. This abstract presents recent advances that have been made on APT data reconstruction, particularly in the areas of algorithm development and field evaporation simulation [3]. Various methods of improving APT reconstruction include: 1) post-reconstruction density correction [4], 2) methods which operate within the limits of the hemispherical projection, both pre- and post-reconstruction [5], and 3) methods which remove the hemispherical limitation, primarily based on simulation [6].

1. T. F. Kelly and D. J. Larson, *MRS Bull.* 37 (2012) 150

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

3. B. P. Geiser et al., *Micro. Microanal.* 15(S2) (2009) 302

4. X. Sauvage et al., *Acta Mater.* 49 (2001) 389, F. Vurpillot, A. Cerezo and D. J. Larson, *Surf. Int. Anal.* 36 (2004) 552, F. DeGeuser et al., *Surf. Int. Anal.*39 (2007) 268.

5. D. J. Larson et al., *J. Microscopy.* 243 (2011) 15, F. Vurpillot et al., *Ultramicroscopy* 111(8) (2011) 1286, B. Gault et al., *Ultramicroscopy* 111(11) (2011) 1619, D. J. Larson et al., *Micro. Microanal.* 17(S2) (2011) 740, M. Moody et al., *Micro. Microanal.* 17 (2011) 226, D. J. Larson et al., *Ultramicroscopy* 111(6) (2011) 506, B. P. Geiser et al., *Micro. Microanal.* (2013) in press,

6. D. J. Larson et al., *Micro. Microanal.* 18(5) (2012) 953, D. Haley et al., *J. Microscopy.* 244 (2011) 170.

8:20am **AP+AS+EM+MI+TF-WeM2 APT Analysis of Superlattices, Nanowires, and Non-Planar Heterostructures**, ***L.J. Lauhon***, Northwestern University **INVITED**

I will describe pulsed laser atom probe tomography of semiconductors and semiconductor heterostructures in which the specimen or device geometry significantly limits the application of alternative analytical characterization techniques, thereby presenting unique opportunities for APT analysis. At the same time, geometry and other factors can complicate specimen preparation and APT interpretation. The talk will present both new scientific findings enabled by APT as well as challenges in data analysis, using three examples. First, I will describe the dopant distribution in semiconductor nanowires, for which APT studies have provided new understanding of dopant incorporation mechanisms. Additionally, advances in nanowire growth and design have enabled imaging of the entire nanowire diameter. Second, I will describe the analysis of InGaN/GaN superlattices extracted from light emitting diodes, for which APT is uniquely able to investigate fluctuations in indium mole fraction and the 3-D morphology of the InGaN quantum wells. In both GaN nanowires and thin-films, we have found that the surface polarity strongly influences the measured stoichiometry, but the indium mole fraction can be determined reliably. Finally, we have analyzed InGaN quantum wells grown on GaN nanowires. These are nonplanar heterostructures in which quantum wells are grown simultaneously on both polar and non-polar surfaces. Data from scanning transmission electron microscopy-based analytical methods will be compared with APT analysis, and the relative merits described. A comparison of these 3 examples will provide insights into the influence of intrinsic materials properties as well as specimen geometry on the capabilities and limitations of APT.

9:00am **AP+AS+EM+MI+TF-WeM4 Atom Probe Analyses of Interfaces in Nd-Fe-B Permanent Magnets for Higher Coercivity**, ***T. Ohkubo**, H. Sepehri-Amin, K. Hono*, National Institute for Materials Science, Japan **INVITED**

Nd-Fe-B permanent magnets are one of the most important engineering materials that are used for traction motors of (hybrid) electric vehicles. For these applications, coercivity at an operating temperature around 200°C must be higher than the demagnetization field in motors; thus, Nd atoms in the $Nd_2Fe_{14}B$ phase are partly substituted with heavy rare earth element (HREE). However, due to the limitation of natural resources of HREE, the development of high coercivity Nd-Fe-B magnets without HREE has become a new technical target in Japan. In order to understand the relationship between the microstructure and the coercivity, quantitative characterization of chemical compositions at various interfaces in Nd-Fe-B magnets have been needed. In this talk, we present how 3DAP analysis results of Nd-Fe-B magnets played crucial role in the development of high coercivity nanocrystalline anisotropy magnets with superior coercivity and comparable energy density.

One of the long-standing issues on the coercivity of Nd-Fe-B sintered magnets was the chemical and magnetic characteristics of the thin intergranular layer that emerge after the optimal post-sinter heat treatment. Although people thought that the intergranular layer is non-ferromagnetic, 3DAP analysis indicated it is ferromagnetic based on the concentration of the Fe within the phase [1]. We also found that the intergranular layer is formed by the Nd/NdCu eutectic reaction. This finding has been applied to nanocrystalline HDDR [2], melt-spun [3], and hot-deformed Nd-Fe-B magnets [4] to modify the grain boundary chemistry by the Nd-Cu eutectic diffusion process. Unlike the conventional HREE grain boundary diffusion process that has to be carried out above 900°C, this new low temperature process suppress the grain growth of the $Nd_2Fe_{14}B$ phase. Employing this new eutectic diffusion process, we have succeeded in developing bulk Nd-Fe-B magnets with sufficiently high coercivity and the energy product comparable to that of the conventional (Nd,Dy)-Fe-B magnets. In this talk, we will emphasize the role of the multi-scale characterization using 3DAP, (S)TEM, and SEM in the development of high coercivity Nd-Fe-B magnets.

This work was in part supported by JST, CREST.

[1] H. Sepehri-Amin, T. Ohkubo, T. Shima, K. Hono, Acta Mater. **60** (2012) 819.

[2] H. Sepehri-Amin, T. Ohkubo, T. Nishiuchi, S. Hirosawa, K. Hono, Scripta Mater. **63** (2010) 1124.

[3] H. Sepehri-Amin, D. Prabhu, M. Hayashi, T. Ohkubo, K. Hioki, A. Hattori, K. Hono, Scripta Mater. **68** (2013) 167.

[4] H. Sepehri-Amin, T. Ohkubo, M. Yano, T. Shoji, A. Kato, T. Schrefl, K. Hono, submitted

10:40am **AP+AS+EM+MI+TF-WeM9 New Insights Into the Corrosion Behavior of Simulated Vitrified Nuclear Waste from Atom Probe Tomography**, *D.K. Schreiber, **J.V. Ryan**, J.J. Neeway,* Pacific Northwest National Laboratory, ***S. Gin***, CEA Marcoule, France

Atom probe tomography (APT) is being used to study the corrosion and alteration layers formed in borosilicate glass samples during long-term (1–26 years) water corrosion. The water environment and glass composition (SON68 – the non-activated surrogate of the French nuclear waste form R7T7 glass) were selected to generate novel insights into the rate-limiting mechanisms of glass corrosion that are relevant to the long-term storage of high-level nuclear waste in a geologic repository. APT concentration profiles across the corroded/pristine glass interface reveal significantly different interfacial widths for B and Na (~2-5 nm) than for Li and H (~15-30 nm), which suggests that multiple element-specific degradation mechanisms are occurring in parallel. Furthermore, the measured interfacial widths are much sharper than were measured previously by energy-filtered transmission electron microscopy and NanoSIMS. Accurate compositional APT analysis of this 26-component complex glass is, however, quite difficult. The implications of these findings and also practical considerations and limitations when performing these experiments will be discussed in some detail.

11:00am **AP+AS+EM+MI+TF-WeM10 Advanced Applications in LEAP Microscopy**, ***H.G. Francois-Saint-Cyr****, R. Ulfig,* CAMECA Instruments, Inc.*, J. Valley, T. Ushikubo,* University of Wisconsin, Madison*, M. Miller,* Oak Ridge National Laboratory*, H. Takamizawa, Y. Shimizu,* Tohoku University, Japan*, L. Gordon, D. Joester,* Northwestern University*, A. Giddings, D. Reinhard, D. Lawrence, P. Clifton, D. Larson*, CAMECA Instruments, Inc.

The second revolution in atom probe tomography (APT), mainly due to the pursuit of sophisticated laser pulsed modes and focused ion beam based sample preparation, has broadened the range of new applications benefiting from three-dimensional, sub-nanometer compositional information [1]. Novel applications include dopant distribution analysis in metal-oxide-semiconductor (MOS) transistor, geological dating of zircon crystals, quantum dot (QD) assembly growth in Light-Emitting Diodes (LEDs), analysis of biological materials, and nano-scale phase behavior of metallic glasses using the LEAP 4000X®.

Elemental mapping from APT allows threshold voltage in 65 nm-node n-MOS transistors to be successfully correlated with the channel dopant concentration [2]. In geology, precipitates containing Y and Pb are visualized after APT reconstruction of zircon crystals and helped understanding the thermal history and mechanisms of mineral reaction, mineral exchange and radiation damage. Data analysis shows that $^{207}Pb/^{206}Pb$ ratios for nm-scale domains (<2x 10^4 atoms Pb) average 0.17±0.04 and 0.43±0.14 for 2.4 and 4.0 Ga zircons respectively [3], in agreement with SIMS ratios (0.1684 and 0.4269) derived from much larger analysis volumes (hundreds of μm^3 (10^{-16} m^3)). In the pillar arrangement of the Quantum Dots (QDs), as imaged in InAs/GaAs multi-layers, the strain field from one QD layer influences the growth of subsequent layers, although the apparent helical distribution has never previously been reported [4]. In biology, spatially organized collagen fibers in the dentin of elephant tusks have been unveiled. Three-dimensional imaging of apatite-derived calcium and phosphate species, inorganic substituents, and carbon/nitrogen containing fragments of organic macromolecules sheds some light on the source of strength for these materials [5]. Metallic glass $Fe_{76}C_{7.0}Si_{3.3}B_{5.0}P_{8.7}Cu_{0.7}$ used for low-cost transformer applications shows phase separation into a -Fe precipitates, ultrafine spheroidal e -Cu-rich precipitates, silicon-depleted $Fe_3(P,B,C)$, and Fe_3C after annealing for 30 minutes at 729 K [6].

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2. H. Takamizawa et al., *Applied Physics Letters* 100 (2012) 253504.

3. J. W. Valley et al., *Abstracts American Geophysical Union Fall Meeting* (2012) V12A-05.

4. A. D. Giddings et al., *Phys. Rev. B* 83 (2011) 205308.

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Part of this research was sponsored by ORNL's Shared Research Equipment (ShaRE) User Facility, which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

11:20am **AP+AS+EM+MI+TF-WeM11 Gaining an Atomic Scale Understanding of Optoelectronic, Magneto- and Ionic-Transport in Nanostructured Materials using Cross-Correlative STEM and APT**, ***B. Gorman****, D. Diercks, R. Kirchhofer*, Colorado School of Mines **INVITED**

Atomic scale characterization of internal interfaces such as grain boundaries and thin films is needed in order to fully understand the electronic, ionic, mechanical, magnetic, and optical properties of the engineered material. High resolution analytical TEM has given a significant amount of new information about these interfaces, but lacks chemical sensitivity below ~1 at% as well as 3-D information and light element sensitivity. Atom probe tomography in inorganic solids has shown that atomic scale, 3-D characterization is possible with 10 ppm chemical resolution, but a thorough understanding of the laser assisted field evaporation process is needed. Previous studies of inorganic photovoltaic devices have shown that APT is capable of quantifying dopant distributions and interface roughness at resolutions where junction models can be directly correlated.

In ionic conductors, grain boundaries are particularly important as they frequently have conductivities at least two orders of magnitude less than the bulk. Therefore, being able to quantitatively characterize the grain boundary nature to ascertain the reasons behind the decreased conductivity is indispensable for guiding future improvements. In this work an oxygen ion conductor $Ce_{1-x}Nd_xO_{2-x/2}$ and a proton conductor $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95}$ were analysed with particular emphasis on analysis of the grain boundary regions. In the Nd-doped ceria, cation and anion segregation at the grain boundary is quantifiable with sub-nm spatial resolution. The BCZY27 specimen was solid state reactive sintered using 2 wt% NiO and then operated in a reducing atmosphere for 1000 hrs. Most grain boundaries were observed to be compositionally no different than the bulk, h owever, some pockets of NiO were found at and near some grain boundaries.

Ferroelectric oxides are used in a wide variety of applications including capacitors, transistors, piezoelectric transducers, and RAM devices. The perovskite family has proven to be especially useful, with materials such as lead zirconium titanate (PZT) and barium titanate (BT) becoming the industry standards in dielectric and multiferroic applications. Through substitutions of niobium or lanthanum for some of the lead, PNZT and PLZT relaxor ferroelectrics are created. They have extraordinarily high piezoelectric and electrostrictive coefficients, respectively making them useful in electromechanical applications. It has been proposed that relaxor ferroelectrics achieve their electrostrictive properties through nanoscale phase separation. APT analysis of these relaxors illustrates that nanoscale phase separation of the B-site cations does occur in volumes less than $20nm^3$.

Atom Probe Tomography Focus Topic
Room: 203 A - Session AP+AS+MI+NS+SS-WeA

APT and FIM Analysis of Catalysts and Nanoscale Materials
Moderator: P.A.J. Bagot, Oxford University, UK

2:00pm **AP+AS+MI+NS+SS-WeA1 Atom Probe Tomography Characterization of Engineered Oxide Multilayered Structures**, ***S.A. Thevuthasan***, *M.I. Nandasiri, A. Devaraj, D.E. Perea, T. Varga, V. Shutthanandan*, Pacific Northwest National Laboratory

There has been growing interest in developing materials which possess high oxygen ionic conduction at low temperatures for solid oxide fuel cell applications. In our group, we have been developing trivalent element doped creia/zirconia multilayer thin film structures for this purpose. We have grown (i) multilayers of high quality samaria doped ceria (SDC) and scandia stabilized zirconia (ScSZ) films, and (ii) samaria and gadolinia co-doped high quality ceria films using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These films exhibit significantly higher oxygen ionic conduction at intermediate temperatures in comparison to bulk materials. Although we have demonstrated that these structures possess high oxygen ionic conduction at low and intermediate temperatures, we haven't established the mechanisms associated with the enhancement in oxygen ionic conduction through these engineered heterogeneous interfaces.

Atom Probe Tomography (APT) can provide quantitative three-dimensional chemical analysis of materials with lateral and depth resolutions in the order of 0.2-0.3 nm and chemical sensitivity up to parts-per-million levels with field-of-view on the order of $100 \times 100 \times 100$ nm^3. Although APT has been extensively used to characterize metals, it is in its infancy in characterizing oxides and insulators. In addition, multilayer structure adds additional complications to the characterization of the doped ceria/zirconia multilayers. In this study, we have synthesized high quality SDC and ScSZ multilayers and used surface impedance spectroscopy to carry out detailed analysis of oxygen ionic conductivity as a function of individual layer thickness and dopant concentration. As a part of this study we attempted coupled scanning transmission electron microscopy and atom probe tomography to study the oxygen vacancy and dopant distributions along with the inter-diffusion and dopant segregation at the interfaces. These STEM/APT findings are correlated to the conductivity measurements and these results will be discussed.

2:20pm **AP+AS+MI+NS+SS-WeA2 Correlative Atom Probe Tomography and Transmission Electron Microscopy of Metal-Dielectric Composites**, ***A. Devaraj***, *R.J. Colby, D.E. Perea, S.A. Thevuthasan*, Pacific Northwest National Laboratory **INVITED**

Metal-dielectric composite materials are ubiquitous in several important engineering applications ranging from catalysis to semiconductor devices. The technological advances in such fields heavily depend upon the development of three-dimensional characterization capabilities that can accurately identify composition and structure at sub-nanometer spatial resolution and ppm-level composition sensitivity. Atom probe tomography (APT) has already demonstrated its potential in three-dimensional characterization of bulk metals and alloys, however the theoretical understanding of the evaporation behavior of dielectrics and metal-dielectric composites, as well as possible artifacts during laser assisted APT, is still at its infancy. 3D transmission electron microscopy (TEM) tomography on the other hand is currently restricted by long acquisition times and reconstruction artifacts. A correlative TEM-APT approach can help in extending the applicability of APT analysis and TEM beyond the current boundaries by providing not only complementary information but also a deeper understanding of the possible artifacts. This presentation will focus on such a correlated TEM-APT approach to investigate the field evaporation behavior of metal dielectric composites with metallic nanoparticles embedded inside oxides as well as planar structures with metallic thin films on single crystalline oxide substrates. Aberration-corrected TEM high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were used to image the APT samples before and after APT analysis. STEM imaging after interrupted APT analysis was used to capture snapshots of evolving tip shape. Such understanding, when combined with novel APT reconstruction processing, can greatly aid in expanding the capabilities of APT analysis to novel complex heterogeneous metal-dielectric composite materials.

3:00pm **AP+AS+MI+NS+SS-WeA4 High Temperature *In Situ* Diffusion Studies of Gas – Solid Reactions with Atom Probe Tomography**, ***S. Dumpala***, *S.R. Broderick,* Iowa State University, *P.A.J. Bagot,* University of Oxford, UK, *K. Rajan*, Iowa State University

The diffusion couples of in-situ metal-oxygen reactions are analyzed through laser pulsed atom probe tomography (APT) reactions and experiments. Using ternary metal compounds, the relative diffusion and segregation of the different species with oxidation is assessed. This provides a further level of information beyond typical diffusion profiles by considering relative changes in metallic species, providing basic material descriptions at a higher resolution then ever previously measured.

The oxidation experiments were performed in-situ and at temperatures of ~450 ^{O}C and at 10^{-3} torr pressures. Given atom probe's atomic scale spatial resolution, chemical diffusion over a nanometers wide range across the chemical interface is assessed with exceptional accuracy, and the identification of compound formation is quantified. By performing all reactions within an in-situ APT reaction cell along with initial (in-situ) cleaning of the samples, any effects due to native oxidation or contamination are eliminated, which is particularly important when considering atomic scale spatial resolution and femto-scale chemical resolution. The challenges associated with performing in-situ reactions and the potential of this new experimental set-up to study a far wider range of treatment conditions, particularly when coupled with a laser-pulsed APT are discussed.

3D results of binary and ternary catalytic alloys are presented and the advancements in studying catalytic reactions are discussed. Aluminum and silicon samples were also oxidized and chemically-mapped atomic scale imaging of the material were processed to identify the preferred stoichiometry of aluminum oxides as a function of the distance from the aluminum-oxygen interface. This demonstrated ability of the APT to simultaneously image and chemically quantify gas-metal interactions at the atomic level enables us to systematically quantify these interactions as a function of material chemistries, crystallographic orientations and important microstructural features.

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4:00pm **AP+AS+MI+NS+SS-WeA7 Atomic Scale Characterisation of Catalyst Material**, ***T. Li***, *P.A.J. Bagot, S.C.E. Tsang, G.D.W. Smith*, Oxford University, UK **INVITED**

Bimetallic heterogeneous catalysts have proven remarkably successful in catalysing a wide range of important processes, in fuel-cells, exhaust emission control and in hydrocarbon processing. However, the effects of the operating environment on the surface composition, structure and stability of the noble metal catalysts are poorly understood at the atomic-scale. This knowledge will be required to produce the improved catalysts needed for future energy- and materials-efficient technologies.

Atom probe tomography offers a unique method for studying these materials, offering atomic-scale chemical identities of the catalyst surfaces and chemisorbed species. We have used APT to show a rich variety of behaviour in Pt-based alloys, investigating the effects of high temperature/pressure oxidation. These reveal pronounced surface segregation behaviour, strongly dependent on the treatment conditions, crystallographic plane and alloy composition. Furthermore, while subsequent reduction treatments remove formed oxides, the marked changes to the metallic surface compositions remain. Such results suggest using sequential oxidation and reduction treatments as an alternative synthesis method for designing and preparing nano catalysts with controlled surface compositions.

Another aspect of our work focuses on the investigation of the use of APT for characterizing catalyst nanoparticles either in colloidal dispersions or on the carbon supports. It is very challenging to fully characterize these complex 3D architectures by conventional electron microscope technique. In this work, we have for the first time demonstrated the use of APT for the analysis and characterization of such materials in atomic detail. Alongside a description of the preparations, we will also present a range of results from these catalysts materials, highlighting the correction between catalytic efficiency and the atomic-scale chemical/structural information uniquely provided by APT.

4:40pm **AP+AS+MI+NS+SS-WeA9 From Field Ion Microscopy of Tips to 3D Atom Probe Tomography of Real Catalyst Nanoparticles*, N. Kruse*, Université Libre de Bruxelles, Belgium** **INVITED**

This contribution will address some major achievements made in the application of Field Ion Microscopy (FIM) and 1D/3D Atom-Probe (AP) techniques to study catalysis-related problems. In particular, we shall demonstrate the unique capabilities of FIM to image reaction-induced morphological reshaping of single metal nanoparticles conditioned in the form of tips. As an example, we show how a nearly hemispherical Rh nanoparticle is transformed into a polyhedral morphology in the presence of oxygen gas.

In a second example, we shall inspect the use of 1D AP as a tool to provide a detailed kinetic analysis of adsorption/thermal desorption processes. As an example, measurements of the mean life time of NO molecules adsorbing on ~ 60 atomic sites of a (111) Pt facet will be presented. A quantitative evaluation of the data in terms of activation energies for desorption along with pre-exponential factors becomes possible by temperature variation.

Third, we shall consider the combined approach of FIM and 1D AP in imaging the dynamics of surface reaction processes while mapping the local chemistry during these processes. As an example, we shall present results of the catalytic reaction between oxygen and hydrogen on the surface of a Rh nanoparticle. Moving reaction fronts are followed here by using video techniques. The observed patterns demonstrate a strong non-linearity merging into oscillating reaction behavior between oxygen and hydrogen. 1D atom-probe measurements during oscillations allow distinguishing between oxygen- and hydrogen-covered surface patches. They also indicate the participation of sub-surface oxygen species in a feedback process. The oscillatory behavior has been successfully modeled using theoretical models of non-linear processes along with DFT.

Finally, we show that 3D AP can also be used for a chemical mapping of single nanosized grains of real catalysts. Using focused ion beam techniques, "CoCuMn" real catalyst particles as used for the selective production of 1-alcohols from synthesis gas (CO/H_2), can be conditioned in the form of tips. A 3D AP analysis of a single catalyst grain demonstrated the occurrence of a core-shell structure with Co forming the core. Interestingly, all three metals are found to be present in a 2nm thick shell which is otherwise dominated by large amounts of Cu. Such information is most important when it comes to establish relationships between catalytic activity/selectivity and surface chemical composition.

5:20pm **AP+AS+MI+NS+SS-WeA11 NO_2 Reduction over Pt and Rh Single Nanoparticles: Imaging with Nanometric Lateral Resolution*, C. Barroo**, S. Lambeets, Y. De Decker, F. Devred, T. Visart de Bocarmé, N. Kruse*,** Université Libre de Bruxelles, Belgium

Nitric oxides (NO_x) emissions from vehicles are harmful to human beings and may cause severe health issues. NO_x abatement is therefore highly desirable, but the development of viable solutions still represents a major challenge for catalyst makers, especially in the case of lean-driven vehicles. NO is known to be oxidized to NO_2 under lean-burn conditions in automotive engines, and subsequently reduced into N_2 during the rich-burn regime. In this work, we have investigated the catalytic reduction of NO_2 over platinum and rhodium field emitter tips by means of Field Emission Microscopy (FEM). Real-time FEM is a powerful method for studying the dynamics of catalytic reactions that take place on the surface of the top of a nanosized metal tip, which acts as a catalytic particle. These studies are performed during the ongoing catalytic reaction which can be imaged in real time and space. Nanoscale resolution is achieved, providing a local indication of the instantaneous surface composition. Reaction-induced structural changes of the catalyst's surface can also be assessed with step-site resolution. FEM is based on the emission of electrons from the sample which can be affected by the presence of various adsorbates. Local variations of the work function are reflected in the form of a brightness pattern and the surface composition of the sample can be qualitatively investigated during the ongoing catalytic process, allowing for the determination of the elementary processes involved.

The microscope is run as an open nanoreactor, through a constant supply of gaseous reactants and constant gas-phase pumping of the reaction chamber, ensuring that the system is kept far from thermodynamic equilibrium. This may lead to non-linear dynamics. Among others, oscillating phenomena observed during the NO_2 reduction by H_2 over both Pt and Rh nanocrystal (whose diameter is ≈40 nm) are presented.

Data have been characterized by Fourier transforms, temporal autocorrelations and dynamical attractors that demonstrate the existence and robustness of the kinetic oscillations. Furthermore, the optimal parameters obtained for the reconstruction of the dynamical attractor from the experimental time series, give important information that can lead to a better understanding of the mechanism of the catalytic reduction of NO_2 over PGM nanoparticles.

5:40pm **AP+AS+MI+NS+SS-WeA12 Quantitative Three-Dimensional Compositional Analysis of Geologic Minerals using Atom-Probe Tomography*, J. Liu,* ***D.E. Perea, R.J. Colby, B. Arey, O. Qafoku, A. Felmy*, Pacific Northwest National Laboratory

Carbon capture and sequestration within deep geological formations has become one of the most important options to mitigate the ever-growing environmental CO_2 emissions. The olivine group of minerals, X_2SiO_4 where X = Mg or Fe, hold promise as potential media to sequester carbon. Upon reaction of supercritical CO_2 (sc-CO_2) with fayalite (Fe_2SiO_4) or forsterite (Mg_2SiO_4), various oxide and carbonate phases result accompanied by a complex change in surface morphology. A combination of atom probe tomography (APT) and scanning transmission electron microscopy (STEM) is being used to map the complex composition across various site-specific interfaces in order to better understand the complex phases that form upon reaction with sc-CO_2. The advantage of APT analysis is that it can provide a unique 3-D atomic-scale compositional map with a part-per-million sensitivity to allow tomographic mapping of low-level impurities such as Li. Optimization of the APT analysis conditions will be discussed leading to the optimal stoichiometric composition. The results demonstrate the viability of using APT analysis to study the composition geological minerals for energy and environmental applications.

*** NSTD Student Award Finalist**

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