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].

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

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.

5. L. M. Gordon, L. Tran and D. Joester, *ACS Nano* 6(12) 2012 10667.

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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 $20nm^3$.

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