Tuesday Afternoon, October 29, 2013

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.

Authors Index

Bold page numbers indicate the presenter