Materials Characterization in the Semiconductor Industry Focus Topic
Room: 313 - Session MC+AP+AS-MoM

Characterization of 3D Structures, 2D films and Interconnects
Moderator: Paul Ronsheim, CTO, PAR Technical Consulting, previously with IBM, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

8:20am **MC+AP+AS-MoM1 Dopant/Carrier and Compositional Profiling for 3D-Structures and Confined Volumes.**, ***Wilfried Vandervorst***, *A. Kumar, J. Demeulemeester, A. Franquet, P. Eyben, J. Bogdanowicz, M. Mannarino, A. Kambham, U. Celano*, IMEC, KU Leuven Belgium **INVITED**

The introduction of three-dimensional devices (FinFets, TFETs and nanowires), has created as new metrology challenges the characterization of dopant /carrier and impurity distributions in 3D-devices and confined volumes. Beyond these dimensional challenges, the use of alternative materials such SiGe, Ge, GeSn alloys as well as III-V materials, adds to the metrology requirements. Recent evolution towards growth (and strain relaxation) mediated by the confined volume (for instance relying on aspect ratio trapping) calls for metrology suited for very small volumes and more atomic scale observations. Metrology in 3D-structures and confined volumes has demonstrated that the changing surface/volume ratios in confined devices versus blanket films lead to phenomena (dopant deactivation, enhanced diffusion,..) which cannot be observed in blanket experiments. Hence more emphasis should be placed on the analysis of device and structures with relevant dimensions relative to the exploration of blanket experiments.

Atomprobe tomography is able to provide composition analysis within very small volumes (a few nm3) with high sensitivity and accuracy and excellent spatial resolution. Hence this enables to observe dopant atom migration in 3D-devices, and through some data mining analysis, even cluster formation as precursor to strain relaxation such as seen in metastable alloys like GeSn. Field Ion Microscopy, a complement to APT, can be used to image impurity atoms clustered around defects within the crystal. Routine application of APT is still hampered by localization problems, reconstruction artifacts due to inhomogeneous evaporation, local magnification effects, sensitivity due to the limited statistics, laser-tip interaction phenomena, etc.

Although scanning spreading resistance microscopy is inherently 2D, analysis of 3D-devices (FinFet, ReRam, Sonos..) is possible by novel approaches such as SPM scalping. The introduction of novel modes such as soft retrace, FFT-SSRM has led of improved resolution and eliminates series resistances resulting from the current confinement in these narrow devices, decoupling the actual “spreading resistance” from the total resistance. Finally SSRM-carrier distribution have been coupled to device simulators leading to an accurate prediction of device performance.

In addition to APT we also present here the concept of “self focusing SIMS” whereby we demonstrate that it is possible to determine, for instance, the SiGe(III-V) composition in trenches as small as 20 nm without having an ion beam with nm-resolution. This represents a significant step forward in terms of production control and statistical relevance.

9:00am **MC+AP+AS-MoM3 Characterization of the Periodicity (Pitch) and Stress of Transistor Fin Structures using X-Ray Diffraction Reciprocal Space Mapping**, ***Alain Diebold***, *M. Medikonda*, SUNY College of Nanoscale Science and Engineering, *M. Wormington*, Jordan Valley Semiconductors Inc

Cleanroom compatible, high resolution X-Ray diffraction systems are now capable of measuring the average pitch and critical dimensions of ordered arrays of fins and the stress state of high mobility layers at the top of the fins. Reciprocal Space Mapping (RSM) characterizes both the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity. The periodicity of the fin arrays has decreased to the point where the fin array adds satellite diffraction peaks to the main Bragg diffraction peak from the semiconductor. The pitch can be calculated from the angular spacing of the satellite peaks. State of the art lithographic processing using the spacer patterning process often results in a different spacing between every other fin. This is known as pitch walking. Pitch walking is very difficult to observed, even using TEM cross-sectional images. The stress state of the high mobility epilayers such as $Si_{1-x}Ge_x$ on Si fins can also be characterized using RSMs. In addition, some of the higher order satellite peaks will split when the fins have a near rectangular shape. This presentation compares the capability of cleanroom and synchrotron based XRD systems for reciprocal space mapping of Si and $Si_{1-x}Ge_x$ / Si transistor fins arrays.[1]

[1] Measurement of Periodicity and Strain in Arrays of Single Crystal Silicon and Pseudomorphic $Si_{1-x}Ge_x$/Si Fin Structures using X-ray Reciprocal Space Maps, M. Medikonda, G. Muthinti, J. Fronheiser, V. Kamineni, M. Wormington, K. Matney, T. Adam, E. Karapetrovaand A.C. Diebold, J. Vac. Sci. Technol**. B32**, (2014), 021804.

9:20am **MC+AP+AS-MoM4 MBE Grading Techniques for the Growth of InAsSb Films with Inherent Properties Unaffected by Strain**, ***Wendy Sarney***, *S.P. Svensson*, US Army Research Laboratory, *Y. Lin, D. Wang, L. Shterengas, D. Donetsky, G. Belenky*, Stony Brook University

By using compositionally graded buffer layers, InAsSb can be grown by molecular beam epitaxy with its inherent lattice properties across the entire composition range. This direct bandgap, III-V alloy is of great interest for infrared detector applications, as it can cover both the mid (3-5 μm) and long wavelength (8-12 μm) bands. The direct bandgap provides the high quantum efficiency that allows it to directly compete with HgCdTe but at potentially much reduced fabrication costs. InAsSb was sidelined for decades, because conventional wisdom indicated its bandgap bowing parameter would not allow it to reach the needed 10-12 μm benchmark. The material was further maligned because it was thought to exhibit CuPt ordering, which affects the bandgap. By revisiting the growth techniques we have determined that the bandgap bowing parameter of InAsSb is more than sufficient for LWIR applications and it can be grown free of ordering, provided that the material is grown with its inherent, undistorted lattice constant.

As there is no perfect substrate available for the InAsSb compositions of interest (typically containing ~40-50% Sb), we grow the films on compositionally graded buffer layers on GaSb substrates. The buffer layers consist of AlGaInSb, GaInSb, or InAsSb grades based on the theories described by J. Tersoff.[1] In this paper we provide experimental verification of Tersoff’s theories applied to ternary and quaternary grades, and for both tensile and compressive grades. Furthermore, the specific parameters calculated by Tersoff, such as the boundary for the dislocation-free region (Zc) is exactly verified by transmission electron microscopy (TEM).

Reciprocal space maps show that the InAsSb layers grown on compositional graded buffer layers have their native lattice constant. The films are free from strain-relieving dislocations within the field of view allowed by TEM. Furthermore, we see no evidence of group V ordering for films grown in this manner. Although ordering is known to further reduce the bandgap, it is a difficult property to control, and it would be very undesirable to rely on it to induce the needed longer wavelengths. We have observed that a finite amount of residual strain that is small enough not to cause dislocation formation can induce CuPt ordering, but this can be completely avoided by using appropriate grading techniques. We also see no evidence of phase segregation or miscibility gaps.

Photoluminescence wavelengths have been measured for numerous InAsSb films, with a maximum wavelength to date of 12.4 μm. This may be the ideal material for direct bandgap infrared device applications.

J. Tersoff, Appl. Phys. Lett. 62, 693 (1993);

9:40am **MC+AP+AS-MoM5 Quantitative 3-D Imaging of Filaments in Hybrid Resistive Memory Devices by Combined XPS and ToF-SIMS Spectroscopies**, *Y. Busby*, ***Jean-Jacques Pireaux***, University of Namur, Belgium

Resistive switching has been observed in a multitude of inorganic (oxides, chalcogenides...) and hybrid (organic or polymers plus metal nanoparticles) thin films simply sandwiched between two metal electrodes. Organic memory devices are particularly promising candidates for developing large scale, high density, cost efficient, non-volatile resistive memories. Their switching mechanism has been for a long time suggested to depend on the formation/rupture of localized conducting paths (filaments). Using electrical characterization by impedance spectroscopy, filament formation has been experimentally demonstrated to be the dominant switching mechanism in many organic memories, only very recently (2014). Otherwise, despite of very dedicated efforts, few experimental techniques have so far succeeded in characterizing and providing information on filament(s).

The present work combines for the first time High Resolution X-Ray induced Photoelectron Spectroscopy (for its quantitative information capability) and Time-of-Flight Secondary Ion Mass Spectrometry (for its very high atomic sensitivity and 3D imaging capabilities) to quantitatively

study both lateral and in depth elements distribution in a complete and operative organic memory device: what happens to be top electrode metal diffusion and filament formation is evidenced and quantitatively evaluated in memory devices which are based on a highly insulating and *cross-linked polystyrene layer*, processed by plasma polymerization, sandwiched between silver and indium tin oxide electrodes. Depth profiles evidence the metal diffusion in pristine and electrically addressed memory elements through the whole organic layer where the silver concentration can reach value as high as 5.10^{19} at/cm^3. Filament formation is shown to be initiated during the top electrode evaporation, and is then successively enhanced by field induced diffusion during the electrical addressing. The 3-D ToF-SIMS images evidenced the formation of metallic paths extending through the entire device depth, electrically bridging the two electrodes when the element is in its low resistance state. Filaments with different characteristics have also been studied in organic memories based on a semiconducting polymer (Polyera N1400 ActiveInk) or on semiconducting small molecules (Tris-(8-hydroxyquinoline)aluminum, AlQ_3). It appears therefore that metallic filaments are indeed at the origin of switching in organic memory devices.

10:00am **MC+AP+AS-MoM6 High Throughput Electron Diffraction-Based Metrology of Nanocrystalline Materials**, *X. Liu,* Carnegie Mellon University, *D. Choi,* Korea Railroad Research Institute, Republic of Korea, *N.T. Nuhfer,* Carnegie Mellon University, *D.L. Yates, T. Sun,* University of Central Florida, *G.S. Rohrer,* Carnegie Mellon University, *K.R. Coffey,* University of Central Florida, ***Katayun Barmak***, Columbia University

The resistivity of Cu, the current interconnect material of choice, increases dramatically as the conductor's dimensions decrease towards and below the mean free path of electrons (39 nm at the room temperature). Two scattering mechanisms that contribute to this resistivity size effect are surface scattering, evidenced by thickness dependence of resistivity, and grain boundary scattering, evidenced by grain size dependence of resistivity. Quantification of microstructural parameters, such as grain size, at the scale of the resistivity size effect necessitates the use of transmission electron microscopy (TEM). In this work, an electron diffraction-based orientation mapping system installed on the TEM is used to characterize not only nanometric Cu films, but also new materials, W, Ni, Ru and Co, that are potential candidates to replace Cu as the next-generation interconnect material. In this characterization technique, spot diffraction patterns are collected as the nano-sized beam scans the area of interest. The crystallographic orientation of each scanned pixel is determined by cross-correlation with pre-calculated diffraction patterns (termed, templates). Precession is used to reduce the dynamical scattering effects, increasing the reliability of the orientation mapping. The raw orientation data is then processed to yield the microstructural data via a well-defined procedure developed to parallel that used to process electron backscatter orientation data taken in scanning electron microscopes. This characterization yields full range of microstructural parameters including grain size, grain size distribution, orientation distribution, misorientation distribution, grain boundary and interface character and plane distribution that are extracted from the crystal orientation maps in a nearly fully-automated manner. These microstructural parameters, along with sample thicknesses, are used to evaluate the validity of the semiclassical resistivity size models for Cu and the new materials, and, where applicable, to determine the relative contributions of surface and grain boundary scattering to the resistivity increase.

10:40am **MC+AP+AS-MoM8 LEIS Characterization of the Outer Surface, Ultra-Thin Layers and Contacts**, ***Hidde Brongersma***, ION-TOF / Tascon / Calipso, Netherlands, *P. Bruener, T. Grehl,* ION-TOF GmbH, Germany, *H.R.J. ter Veen*, Tascon GmbH, Germany **INVITED**

Modern day technologies are increasingly based on high performance nanomaterials and novel preparation techniques for such materials are developed at a rapid pace. Advances in nanoscience and nanotechnology heavily rely on the availability of analytic techniques that can validate and support new nanomaterials synthesis procedures. With the introducing of the Qtac^{100}, a new high-sensitivity Low Energy Ion Scattering (HS-LEIS) instrument, one can quantitatively analyze the atomic composition of the surface of a wide range of materials with an unparalleled surface sensitivity.

The outermost atoms of a surface largely control processes such as growth, nucleation, poisoning, adhesion and electron emission. While analytic tools (such as XPS) probe an average of many atomic layers, LEIS can selectively analyze the outer atoms. In addition, non-destructive in-depth information, with high depth resolution, is obtained for the heavier elements (0 - 10 nm). HS-LEIS is just as well suited for the *quantitative analysis* of amorphous, insulating and extremely rough surfaces as for flat single crystals. Since HS-LEIS is a fast analysis technique, it can be used to follow diffusion processes in-situ.

The focus will be on applications where valuable information has been obtained that is impossible (or very difficult) to obtain with other analytical techniques. The unique possibilities will be illustrated with state-of-the-art applications for: ALD growth of ultra-thin layers, surface modification, interface diffusion, core/shell nanoparticles, graphene, self-assembled monolayers for sensors.

The findings will be compared and contrasted to those obtained by other analytic techniques such as XPS, Auger, SIMS, RBS and conventional LEIS.

11:20am **MC+AP+AS-MoM10 Backside versus Frontside Characterization of High-k/Metal Gate Stacks for CMOS sub-14 nm Technological Nodes**, ***Eugenie Martinez***, CEA, LETI, MINATEC Campus, France, *B. Saidi, P. Caubet, F. Piallat,* STMicroelectronics, France, *H. Kim,* CEA, LETI, MINATEC Campus, France, *S. Schamm-Chardon,* CEMES-CNRS, France, *R. Gassilloud*, CEA, LETI, MINATEC Campus, France

Down-scaling of CMOS transistors beyond the 14 nm technological node requires the implementation of new architectures and materials. The gate last integration scheme is a promising solution to better control the threshold voltage of future MOSFETs, because of its low thermal budget [1]. Advanced characterization methods are needed to gain information about the chemical composition of such structures. The analysis of thin layers and interfaces buried under a thick metal electrode is particularly challenging. An effective approach based on backside sample preparation is proposed here.

To tune the work-function toward nMOS values, the technology currently investigated is based on HfO_2 for the dielectric and a thin TiN layer capped by a TiAl alloy for the gate [2]. For a better understanding of aluminium and other elements redistributions after a 400°C annealing, a specific methodology has been developed based on the removal of the Si substrate. It allows to achieve XPS and Auger analyses from the backside of the sample [3].

In particular, Auger depth profiling performed on HfO_2/TiN/TiAl/TiN/W gate stacks at low energy (500 eV Ar^+) brought the following main conclusions: a) no Al diffusion toward the HfO_2/TiN interface, b) nitrogen out diffusion in the upper TiAl film, c) significant oxygen scavenging. By comparison, these results evidenced that Auger frontside analyses suffer from sputter-induced artifacts.

In a further study, to understand the behavior of nitrogen out diffusion in the TiAl layer, we deposited $TiAlN_x$ thin films with various nitrogen flows by reactive sputtering deposition and performed backside XPS analyses. At low/medium nitrogen flows, which correspond to the $TiAlN_x$ film after TiN/TiAl bilayer anneal, the N1s core level spectra obviously shows that N is mainly bonded to Al rather than Ti. Results are compared with frontside XPS performed with a thinner TiN upper layer. The backside approach is shown to be more representative of the technological stack, in particular with respect to the TiN oxidation.

Measurements were carried out at the NanoCharacterization Platform (PFNC) of MINATEC.

[1] C. L. Hinkle et al., Appl. Phys. Let. 100, 153501 (2012).

[2] A. Veloso et al.., Symposium on VLSI Technology, Digest of Technical Papers (2011).

[3] M. Py et al., AIP conference proceedings 1395, 171 (2011).

11:40am **MC+AP+AS-MoM11 Charge Storage Properties of Al/(1-x)$BaTiO_{3-x}Ba(Cu_{1/3}Nb_{2/3})O_3$ (x = 0.025) (BTBCN)/HfO_2/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices**, ***Souvik Kundu***, *M. Clavel, D. Maurya, M. Hudait, S. Priya*, Virginia Tech

Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed laser deposited 300 nm (1-x)$BaTiO_{3-x}Ba(Cu_{1/3}Nb_{2/3})O_3$ (x = 0.025) (BTBCN) ferroelectric film and atomic layer deposited 10 nm HfO_2 insulating layer on silicon semiconductor substrate were developed for next generation ferroelectric non-volatile memory applications. For the first time, the structural, interfacial, and electrical properties of these Al/BTBCN/HfO_2/p-Si MFIS devices were studied, and the role of BTBCN as charge storing elements was also established. The X-ray diffraction and transmission electron micrograph with selected area diffraction pattern clearly demonstrate the single crystallization of BTBCN ferroelectric films. It was found that insertion of 10 nm HfO_2 in-between BTBCN and Si improves the interfacial properties and also prevents the interdiffusion of semiconductor into the ferroelectric layer. The optical bandgap of BTBCN was found to be 4.38 eV using transmission spectrum analysis. The MFIS structure showed capacitance-voltage hysteresis loops due to the ferroelectric polarization of BTBCN and the maximum memory window was found to be 1.65 V when the sweeping voltage was ±10 V. However, no memory window was found in metal-insulator-semiconductor devices, i.e., when there is no BTBCN layer in between metal and insulating layer. The leakage current of these devices was found to be 7×10^{-9} A/cm^2 at an applied voltage of -1 V. The wide memory window and superior retention

properties were achieved due to the presence of BTBCN. The electronic band diagrams of these MFIS devices during program and erase operations were proposed.

Keywords: BTBCN; MFIS; Memory window; Leakage current; Band-diagram

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 313 - Session MC+2D+AP+AS-MoA

Characterization of III-Vs (2:00-3:20 pm)/Photovoltaics, EUV masks, etc. (3:40-4:40 pm)
Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

2:00pm **MC+2D+AP+AS-MoA1 High Resolution SIMS Depth Profiling in III-V Compound Semiconductors**, ***Marinus Hopstaken***, *M.S. Schamis, Y. Sun, A. Majumdar, C.-W. Cheng, B.A. Wacaser, G. Cohen, K.K. Chan, D.K. Sadana, D.-G. Park, E. Leobandung*, IBM T.J. Watson Research Center

Recently, there has been renewed technological interest for application of InGaAs and related III-V high-mobility materials as a potential replacement for the MOSFET Si-channel [1]. Successful integration of novel materials and processes requires accurate physical characterization of in-depth chemical distribution with nm-scale resolution. We will address some of the challenges regarding SIMS depth profiling of III-V materials and propose analytical solutions for the characterization of more complex multilayer substrates, impurities therein, and Ultra-Shallow Junction (USJ) doping profiles.

Ion beam based sputtering of III-V compounds is intrinsically more complex than in conventional Si substrates. One of the major issues with depth profiling of III-V materials is their higher sensitivity to formation of ion-beam induced topography, which has a detrimental impact on depth resolution [2]. We have previously reported anomalous sputtering behavior of (In)GaAs under low energy O_2^+ sputtering, causing severe degradation of depth resolution [3].

In case of low energy Cs^+ sputtering at oblique incidence, we have achieved uniform sputtering conditions on different III-V compounds with no significant topography formation. We have demonstrated constant depth resolution in III-V multilayer structures with decay lengths as low as 2 nm/decade at low Cs^+ impact energy (down to 250 eV).

We will address some of the analytical challenges regarding the quantification of depth and concentration scales in III-V multilayer structures, grown by hetero-epitaxy. We employ explicit corrections for yield variations using appropriate standards in their respective matrices. A special case occurs for the group IV *n*-type dopants (*i.e.* Si, Ge), which are typically monitored as negative cluster ion attached to the group V element for reasons of sensitivity. We have developed a quantification scheme to determine [Si] doping profiles in hetero-epitaxial structures, composed from the negative cluster ions (e.g. $SiAs^-$, SiP^-) in the respective matrices.

In summary, this work has improved our fundamental understanding of low-energy ion beam interactions in III-V materials, which is essential for achieving sub-nm depth resolution in thin-film structures. In addition, this work has provided with an optimum window of analytical conditions for quantitative analysis of a wide variety of impurities and dopants with high sensitivity in different III-V materials.

1. Y. Sun et al., *IEDM 2013 Conf. Proc*., p. 48-51.

2. E.-H. Cirlin, J. J. Vajo, R. E. Doty, and T. C. Hasenberg, *J. Vac. Sci. Technol. A***9**, 1395 (1991).

3. M. J. P. Hopstaken et al., *J. Vac. Sci. Technol. B***28**,1287, (2012).

2:20pm **MC+2D+AP+AS-MoA2 Nitrogen Incorporation in Dilute Nitride III-V Semiconductors Measured by Resonant Nuclear Reaction Analysis and Ion Beam Channeling**, ***John Demaree***, *S.P. Svensson, W.L. Sarney*, US Army Research Laboratory

The behavior of dilute nitride III-V semiconductors depends critically on the number of nitrogen atoms residing substitutionally on Group V sites, and this small nitrogen incorporation may be used to tailor the optical bandgap for detection of electromagnetic radiation in future low-cost near-infrared imaging systems. In this study, films of GaAsN and GaSbN were synthesized using molecular beam epitaxy at various temperatures and growth rates, with the assistance of a nitrogen plasma source isotopically enriched with ^{15}N. The films were examined using x-ray diffraction, secondary ion mass spectroscopy, x-ray photoelectron spectroscopy, and resonant nuclear reaction analysis (RNRA) to assess the amount of nitrogen incorporation. Furthermore, RNRA measurements were combined with ion beam channeling methods to ascertain the fraction of incorporated nitrogen atoms residing on substitutional and interstitial lattice sites. The narrow energy resonance and corresponding high depth resolution of the nuclear reaction used (the 897 keV p,gamma reaction with ^{15}N) also enabled an assessment of the substitutional incorporation of the nitrogen throughout the thickness of the 100-400 nm thick films.

2:40pm **MC+2D+AP+AS-MoA3 Determination of Growth Conditions for Highly Mismatched Alloys, Using *In Situ* Auger Electron Spectroscopy and Flux grading**, ***Stefan Svensson***, *W.L. Sarney*, US Army Research Laboratory, *M. Ting, K.M. Yu,* Lawrence Berkeley National Laboratory, *L.W. Calley*, Staib Instruments, Inc.

The electronic band structures of GaN can be effectively modified by the incorporation of Sb. Because of the high electronegativity mismatch between Sb and N growth of GaNSb by molecular beam epitaxy (MBE) must be done at relatively low temperatures and under N-rich condition in order to control the bandgap of the material. The Sb-flux must also be chosen carefully in relation to the growth rate and N-overpressure to control composition and crystallinity. These growth conditions represent a vast parameter space, which is extremely time-consuming to explore in a systematic fashion.

The typical approach for attacking such a problem is to judiciously select a limited set of parameter combinations based on experience and literature data. However, if growth windows are narrow there is no guarantee for success. To more quickly cover a larger parameter range we have grown a very limited number of samples but continuously varied one parameter at a time while employing a combination of in situ and ex situ probes that can reveal critical parameter points. The most novel piece of equipment is the in situ *STAIB Auger Probe,* which allows uninterrupted chemical analysis during crystal growth. In all of the following experiments the substrate temperature was fixed at 325 °C.

In one experiment we determined the transition between Ga- and N-rich MBE growth conditions of GaN by setting a fixed N-flow that generated a steady-state background chamber pressure of $1.5x10^{-5}$ Torr, while the Ga-source was set up to generate a linear flux ramp from $9.8x10^{16}$ to $3.9x10^{18}$ at/m^2/s over two hours. During this ramp, the Auger electron signals for N (375 eV), and Ga (1050 eV) were continuously monitored. As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N- and Ga-rich conditions and could thus determine the critical Ga-flux relative to the N gas-flow.

In a second experiment the previous information was used to set Ga- and N-fluxes to slight N-rich conditions, while the Sb-valve was slowly opened. In this case both the Auger signals and the reflection high-energy electron diffraction pattern were observed to find the transition between crystalline and amorphous growth conditions. The sample was subsequently analyzed with Rutherford backscattering, which verified the varying Sb-composition. With the data from these two test samples subsequent films were grown with the desired bandgap of 2.2 eV suitable as photoelectrodes for photoelectrochemical water splitting application.

3:00pm **MC+2D+AP+AS-MoA4 Electron Channeling Contrast Imaging: Examining Dislocation Effects in III-Ns**, *J.K. Hite*, U.S. Naval Research Laboratory, *P. Gaddipati*, American Society for Engineering Education, ***Michael Mastro***, *C.R. Eddy, D.J. Meyer*, U.S. Naval Research Laboratory

III-N materials continue to play a significant role in a range of technologies from rf electronics to visible and UV emitters and detectors. This is true despite a heavy population of extended defects in the active regions of these devices, which degrade the operation, potential performance, and reliability of such devices. With such high dislocation densities when grown heteroepitaxially on sapphire or SiC (10^8-10^{10} cm^{-2}), techniques to reliably, rapidly, and non-destructively determine spatially defect density are necessary to determine the effects of these defects on device performance.

The most precise characterization tool for defect density has been transmission electron microscopy, but this is a destructive technique, as are other methods such as molten KOH or photo-electrochemical etching of the surface to reveal dislocation sites. Cathodoluminescence imaging only detects dislocations which change the optical emission of the material. X-ray diffraction can be used to extrapolate dislocation density, but not identify individual defects.

Electron channeling contrast imaging (ECCI), a non-destructive technique that has been used to examine defects in metals and ceramics, has recently seen use in III-nitride semiconductors. This technique allows for direct imaging of dislocations, grain boundaries, and topological information all at once. We will present an overview of the uses of ECCI in characterizing III-

N materials, culminating in recent work applying the technique to AlGaN/GaN HEMT structures. By imaging the active areas of van der Pauw structures on a single sample with varying mobility, we find a direct negative correlation between screw dislocation and electron mobility.

3:40pm **MC+2D+AP+AS-MoA6 EUV Lithography Mask Cleaning Applications of TOF SIMS Analysis**, ***Thomas Laursen***, *S.W. Novak,* SUNY College of Nanoscale Science and Engineering, *A. Rastegar,* SEMATECH, *T. Nakayama*, SUNY College of Nanoscale Science and Engineering

Extreme-UV Lithography (EUVL) is the current R&D frontier for the semiconductor industry. Developing this new technology is generating new studies into a range of new materials issues. EUVL photomask is one important branch of this technology and serious issues have been identified related to the mask surfaces. Photomask performance is usually characterized in terms of EUV (λ = 13.5 nm) Reflectivity (EUVR) and absorption. But when it comes to surface degradation by radiation exposure and mask cleaning of defects, it is valuable to complement EUVR with a surface analytical technique in order to elucidate the material changes taking place. TOF SIMS has proven to be a versatile analytical technique in this regard. While it may not be the optimal technique in each and every case, it does provide high sensitivity to compositional changes and high-resolution depth profiles. Furthermore, TOF-SIMS analysis on the IonTof V-300 can be done using full-size photomasks which allow analysis at the various stages of processing.

The surface structures on the EUV mask surface consist of a stack of thin films having thicknesses ranging from 1 to 50 nm. The reflective layer contains 40 bilayers of Mo-Si consisting of 2.7 nm Mo and 4.1 nm Si—ending with a Si layer. This multilayer is usually capped with either a 2.5 nm Ru or in some cases a 2 nm TiO_2 surface film. Metallic films with high extinction coefficient with thicknesses in the range from 35 to 75 nm are deposited as an absorber layer and patterned on Ru-capped multilayer blanks.

The combination of EUVR and TOF-SIMS analysis of the Ru capped multilayer EUV masks and blanks provided detailed information on the effects of cleaning on contamination, materials degradation and oxidation. Whereas the EUVR measurements could be directly related to mask specifications, the TOF-SIMS analysis provided more detailed information on surface contamination and oxidation levels, as well as surface-film integrity.

The interactions of the various segments constituting a cleaning process have been characterized in terms of their effect on film etching and removals as well as film oxidation. In general sulfuric acid - H2O2 -based treatments caused a severe deterioration of the film structures, whereas NH4OH - H2O2 -based treatments (SC1) caused a more manageable deterioration. Current mask cleaning processes are therefore primarily based on SC1 cleaning. Another concern for mask defectivity is progressive defects generated by sulfate and ammonium compounds. TOF-SIMS was also used to study the aggregation of these compounds during electron irradiation (simulating EUV-irradiation conditions), which was visualized by stage-scan imaging.

4:00pm **MC+2D+AP+AS-MoA7 Characterization of Ag/CuInSe$_2$ Thin-Film Photovoltaics by Photoelectron Spectroscopy**, ***Pinar Aydogan***, Bilkent University, Turkey, *N. Johnson, A. Rockett,* University of Illinois at Urbana-Champaign, *S. Suzer*, Bilkent University, Turkey

Photovoltaic power source technology is one of the most desirable ways to provide energy for the world of tomorrow. Hence, it is important to understand the surface, electrical and photo-induced properties of these materials in order to enhance their efficiencies. Currently used materials in photovoltaic manufacturing technology are mainly crystalline silicon, CdTe (cadmium telluride), amorphous and nanocrystalline silicon, CIS (copper indium diselenide) and CIGS (copper indium gallium selenide). In this study, we focused only on the silver/copper indium diselenide cells, which contain a CdS layer on top. X-ray photoelectron spectroscopy (XPS) that we used for analysis was modified to apply both an external photo illumination and voltage bias during data acquisition. The first part of the research focuses on the result of photo induced variations in binding energies of elements and the main objective is to understand the different binding energy shifts of each element in the Ag/$CuInSe_2$ films in both wavelength- and intensity-sensitive fashion under illumination with three different continuous wave lasers. Furthermore, electrical charging properties of CIS/CdS thin film are studied with externally applied electrical square-wave pulses (SQW), so-called Dynamic XPS. Results will be presented with an ultimate aim of better understanding of the roles of defects affecting the performance of CIS devices. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

4:40pm **MC+2D+AP+AS-MoA9 Facile Synthesis of Composition Tuned $Cu_{1-x}Zn_xO$ Nanoarchitecture on Alpha-Brass**, *Y. Myung*, ***Sriya Banerjee,*** Washington University, St. Louis, *H. Im, J. Park,* Korea University, *S. Raman,* Physical Electronics Inc., *P. Banerjee*, Washington University, St. Louis

Composition controlled $Cu_{1-x}Zn_xO$ layers have been synthesized on pretreated a-brass followed by ambient oxidation. The pretreatment consists of a vacuum anneal step which effectively depletes the surface of Zn. The depleted Zn specimens were then oxidized at various temperatures ranging from 300°C – 600°C. SEM and XRD result shows the oxide consists of CuO/ZnO film/nanowire composite architecture. The analysis of electronic structure (XPS) and optical properties (PL) shows the formation of Zn containing alloy in the surface region of CuO films. The composition ratio of Cu and Zn were calculated based on XPS survey spectra. In particular, XPS fine spectra revealed that as the oxidation temperature increases, the binding energy of Zn $2p_{3/2}$shifts to higher energy, suggesting the possibility of hybridization between the Zn ions and Cu ions.

Photoelectrochemical properties of $Cu_{1-x}Zn_xO$ cathodes exhibit robust photocurrent densities (~3 mA/cm^2). We suggest the dezincification followed by thermal oxidation provides a better approach for composition tuned nanostructure design and fabrication. These semiconductor nanoarchitectures are excellent candidate materials for fabricating solar energy harvesting photoelectrodes as well as optoelectronic devices.

5:00pm **MC+2D+AP+AS-MoA10 In-line Dimensional Measurement via Simultaneous Small Spot XPS and XRF for Cu CMP Process Control**, *B. Lherron,* ST Microelectronics, ***Wei Ti Lee***, Revera, *Motoyama, Chao, Deprospo, Kim*, IBM

As Cu lines used for CMOS devices interconnections become thinner and smaller, current metrology solutions reach their limits. XRay Photoelectron Spectroscopy (XPS) and XRay Fluorescence (XRF) are commonly used as Semiconductor manufacturing process control techniques to measure composition and/or film thickness. In this paper we are exploring the use of a combination of XPS and XRF collected simultaneously to measure the dimensions (line top CD, area and thickness) of Cu lines post Cu CMP on patterned structures. A set of structures with different Cu line width and pitch were used to demonstrate the capability of XPS/XRF on this new application. Results obtained showed good correlation with predicted CD measured by XPS and line section measured by XRF .The paper will also present the comparison with cross section as well as the performance in precision, sensitivity and accuracy of the newly developed technique.

This work was performed by the Research and Development Alliance Teams at various IBM Research and Development Facilities

5:20pm **MC+2D+AP+AS-MoA11 Imaging of the Native Inversion Layer on Silicon-on-Insulator via Scanning Surface Photovoltage; Implications for RF harmonic generation**, ***Daminda Dahanayaka***, IBM, *A. Wong,* Dartmouth College, *P. Kaszuba, L. Moszkowicz, R. Wells, F. Alwine,* IBM, *L.A. Bumm,* University of Oklahoma, *R. Phelps, J. Slinkman*, IBM

Imaging of the native inversion layer on Silicon-on-Insulator via Scanning Surface Photovoltage;

Implications for RF harmonic generation

Daminda Dahanayaka[1], Andrew Wong[2], Phil Kaszuba[1], Leon Moszkowicz[1], Randall Wells[1], Frank Alwine[1], Lloyd A. Bumm[3], Richard Phelps[1] and James Slinkman[1]

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One of the major challenges encountered during the development of IBM's state-of-the-art RF CMOS Technology on Silicon-on-Insulator (SOI) was to overcome the adverse effects on the harmonic performance of stacked switch devices and transmission lines due to the presence of trapped positive charge, Q^+, at the interface of the buried oxide (BOX) and the underlying high-resistivity substrate (SX). Most commercially available standard SOI substrates for RF applications have specifications to maintain Q^+ less than 10^{11} cm^{-2}. The substrate resistivity for IBMs technology is specified to be greater than 1000 ohm-cm, (p-type), i.e. $p_0 \approx 5 \times 10^{13}$ cm^{-3}. This combination induces a "built-in" n-type inversion layer just under the BOX/SX interface. Using "Scanning Surface Photovoltage" (SSPV) microscopy, we present the first data to show quantitatively the extent of this inversion layer into the substrate. The technique disclosed here quantifies the inversion layer, the degree to which it can be suppressed, and

has led to further enhancements to the RF technology on SOI, such as substantial NFET off-state leakage reduction.

References

[1] A. Botula et al., IEEE Topical Meeting on Silicon Monolithic Integrated Circuits in RF Systems, 2009. SiRF '09, 1-4 (2009).

[2] L.A. Bumm et al., US Patent No. 7,944,550.

[3] T. Ohno,IEDMTech. Digest, 627-630 (1995).

[4] J. Greco et al., US Patent No. 8299537 B2.

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+MC+NS+SS-ThM

APT Analysis of Semiconductors, Magnetic and Oxide Materials

Moderator: Paul Bagot, Oxford University, UK, Daniel Perea, Pacific Northwest National Laboratory

8:00am **AP+AS+MC+NS+SS-ThM1 A Vision for Atom Probe Tomography**, ***Thomas F. Kelly***, CAMECA Instruments Inc **INVITED**

Atom Probe Tomography has undergone revolutionary changes in the past two decades. It is tempting to think that these changes are likely to be followed by a period of adjustment and maturation but not continued innovation. However, there are still many active opportunities for development of atom probe tomography. Some of these new technologies are already upon us. There are recent major developments in data reconstruction, detector technology, data mining, and correlative microscopy. Furthermore, application areas are evolving at a rapid pace. The equipment needed to serve some applications will necessarily be developing alongside the more fundamental operating components of atom probes.

This talk with review some recent developments that are just emerging and will offer a vision for where the field is headed. Some of the unproven concepts needed to reach this vision will be highlighted.

8:40am **AP+AS+MC+NS+SS-ThM3 Interfaces in Semiconductors: Application to Photovoltaic Materials**, ***Oana Cojocaru-Mirédin***, Max Planck Institut fur Eisenforschung GmbH, Germany, *R. Würz,* Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Germany, *D. Raabe*, Max Planck Institut fur Eisenforschung GmbH, Germany **INVITED**

$Cu(In,Ga)Se_2$ (CIGS), $Cu_2ZnSnSe_4$ (CZTSe), and multicrystalline Si (mc-Si) solar cells possess a high efficiency [1], despite the polycrystalline structure of the absorber layer. One of the major factors controlling the cell efficiency is the diffusion of the impurities during the fabrication process into the absorber layer and to the p-n junction [2]. However, the interaction between the defects and the impurities at the internal interfaces is not completely understood. This is due to a lack of information on the local chemical changes across the internal interfaces at the nanoscale.

As a step towards a better understanding of the impurity redistribution at the internal interfaces, we have developed novel approaches of preparing site-specific atom probe specimens using combined focused ion beam (FIB), (scanning) transmission electron microscopy ((S)TEM) and electron backscattered diffraction (EBSD). These approaches allow selected GBs in polycrystalline CIGS, CZTSe and mc-Si layers to be studied by atom probe tomography (APT).

Several examples of correlative EBSD-TEM-APT (see Figure 1) and STEM-APT (see Figure 2) studies will be presented in this work. Using APT, segregation of impurities at the GBs was directly observed. APT data of various types of GBs will be presented and discussed with respect to the possible effects on the cell efficiency.

[1] Empa [Internet]. Empa.ch: A new world record for solar cell efficiency, 2013. Available from: http://www.empa.ch/plugin/template/empa/3/131438/---/l=2 [cited 2013 January 18].

[2] J. L. Shay, S. Wagner, H. M. Kasper, Appl. Phys. Lett. 27 (1975) 89, S. Yip and I. Shih, Proceedings of the 1st World Conference on Photovoltaic Energy Conversion (IEEE, Piscataway, 1994), p.210.

9:20am **AP+AS+MC+NS+SS-ThM5 Analysis of Discontinuous InGaN Quantum Wells by Correlated Atom Probe Tomography, Micro-Photoluminescence, and X-ray Diffraction**, *J. Riley, X. Ren,* Northwestern University, *D. Koleske,* Sandia National Laboratories, ***Lincoln Lauhon***, Northwestern University

In(x)Ga(1-x)N quantum wells are the foundation of solid-state lighting, with excellent quantum efficiencies despite high densities of defects. While there is as yet no universally accepted explanation for the high-efficiency, it is clear that carrier localization plays a role. Consistent with this picture, the quantum efficiencies of some samples can be improved by annealing and hydrogen gas to produce discontinuous quantum wells. However, the standard analysis of quantum well widths and composition by high-resolution x-ray diffraction is complicated by such complex morphologies. Specifically, the influence of surface roughness, and interfacial diffuseness, and planar continuity may be difficult to deconcolve. We will describe correlated analysis of continuous and discontinuous InGaN quantum wells by atom probe tomography, micro-photoluminescence, high-resolution x-ray diffraction, and atomic force microscopy. We find that precise composition profiles extracted from atom probe analysis enable refinement of x-ray diffraction peak fitting in the case of continuous quantum wells, and a better estimate of indium mole fraction and quantum well width. For discontinuous quantum wells, atom probe analysis enables simple models to be integrated into routine x-ray diffraction modeling to enable reliable extraction of indium mole fraction and better correlation with photoluminescence spectra. Correlation of atomic force microscopy tomographic images and micro-photoluminescence spectra over common sample areas, together with site-specific lift out techniques, will be presented to explore the surprising coexistence of high quantum efficiency and inhomogeneous broadening due to the complex underlying quantum well morphology.

9:40am **AP+AS+MC+NS+SS-ThM6 Atom Probe Tomography Characterization of Doped Epitaxial Oxide Multi-Layered Structures**, ***Nitesh Madaan***, *A. Devaraj, Z. Xu, M.I. Nandasiri, S.A. Thevuthasan*, Pacific Northwest National Laboratory

Atom probe tomography is the state of the art 3D microscopy technique with sub-nanometer scale spatial resolution and ppm level mass sensitivity. For complex heterogeneous materials the accurate artifact-free reconstruction of collected data is quite a challenging task due to varying local evaporation fields leading to non-hemispherical evolution in the tip shape during the APT analysis. In this work we utilized laser assisted APT to analyze alternate multilayer oxide thin film structure of Samaria doped ceria (SDC) and Scandia stabilized zirconia (ScSZ), grown epitaxially on sapphire substrate, which is potentially useful for solid oxide fuel cells due to their high ionic conductivity. By analyzing the sample in different orientations (top-down, side-ways, and back-side) and comparing with dynamic tip shape evolution using level set simulations for similar geometries, an attempt was made to understand and decouple the APT evaporation artifacts from the real physical sample features. This study would help provide insights to improve the APT reconstruction process for complex multi-layered thin film materials.

11:00am **AP+AS+MC+NS+SS-ThM10 Atom Probe Tomography and Field Evaporation of Insulators and Semiconductors: Theoretical Issues**, ***Hans Kreuzer***, Dalhousie University, Canada **INVITED**

After reviewing the physics and chemistry in high electrostatic fields and summarizing the theoretical results for Atom Probe Tomography of metallic tips, we turn to the new challenges associated with insulators and semiconductors with regard to local fields inside and on the surface of such materials. The recent (theoretical) discovery that in high fields the band gap in these materials is drastically reduced to the point where at the evaporation field strength it vanishes will be crucial in our discussion.

11:40am **AP+AS+MC+NS+SS-ThM12 Atom Probe Tomography Investigation of the Microstructure of Multistage Annealed Nanocrystalline $SmCo_2Fe_2B$ Alloy with Enhanced Magnetic Properties**, ***Xiujuan Jiang***, *A. Devaraj,* Pacific Northwest National Laboratory, *B. Balamurugan,* University of Nebraska-Lincoln, *J. Cui,* Pacific Northwest National Laboratory, *J. Shield*, University of Nebraska-Lincoln

Permanent magnets have garnered great research interest for energy applications. The microstructure and chemistry of a permanent magnet candidate—$SmCo_2Fe_2B$ melt-spun alloy—after multistage annealing was investigated using high resolution transmission electron microscopy (HRTEM) and atom probe tomography. The multistage annealing resulted in an increase in both the coercivity and magnetization as is desired for permanent magnets design. The presence of $Sm(Co,Fe)_4B$ (1:4:1) and $Sm_2(Co,Fe)_{17}B_x$ (2:17:x) magnetic phases were confirmed using both techniques. Fe_2B at a scale of ~ 5 nm was found by HRTEM precipitating within the 1:4:1 phase after the second-stage annealing. Ordering within the 2:17:x phase was directly identified both by the presence of antiphase boundaries observed by TEM and the interconnected isocomposition surface network found in 3D atom probe results in addition to radial distribution function analysis. These observed variations in the local chemistry after the secondary annealing were considered pivotal in improving the magnetic properties.

12:00pm **AP+AS+MC+NS+SS-ThM13 Detector Dead-time Effects on the Accurate Measurement of Boron in Atom Probe Tomography**, ***Frederick Meisenkothen***, National Institute of Standards and Technology (NIST), *T.J. Prosa*, CAMECA Instruments Inc., *E.B. Steel*, NIST, *R.P. Kolli*, University of Maryland, College Park

The atom probe tomography (APT) instrument uses a time-of-flight (TOF) mass spectrometer to identify ions that are field ionized and evaporated from the apex of a needle-like nano-tip specimen. A pulse event, either laser or voltage, is used to trigger field evaporation and to initiate the timing sequence for the mass spectrometer. Ideally, a single atom is field evaporated during a single pulse event. However, it is also common to have multi-hit detection events where more than one ion strikes the detector between pulses. For reasons not completely understood, some elements, such as boron, are prone to field evaporate in multi-hit detection events when compared to other elements, and a large fraction of the boron signal is reportedly lost during acquisition. Obtaining an improved understanding of the field evaporation behavior of boron at different concentration levels, in view of the limited ability of the detection system to resolve multi-hit detection events, may lead to new ways to compensate for the boron signal loss.

A nominally pure boron sample was chosen as a high boron concentration material while the boron implanted silicon, NIST-SRM2137, (1E15 atoms cm^{-2} retained dose) was chosen as the low boron concentration material. A dual-beam FIB/SEM instrument, with an *insitu* lift-out system, was used to prepare the APT specimen tips from the bulk materials. A laser pulsed LEAP 4000X Si* instrument was used to acquire APT data sets for each of the specimen tips. Custom software scripts were used to filter the data sets and extract the ion information associated with specific search criteria, e.g. event multiplicity, which is the number of ions within a given multi-hit event. Ion correlation analysis was used to graphically demonstrate the detector dead-time effect. In the present work, more than 60% of the detected boron signal resided within the multi-hit detection events, for both the high and low boron concentration samples.

* Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+EN+NS+SS-ThA

APT and FIM Analysis of Catalysts and Nanomaterials

Moderator: David Diercks, Colorado School of Mines, David Larson, CAMECA Instruments Inc.

2:20pm **AP+AS+EN+NS+SS-ThA1 *In Situ* Study of Gas - Solid Reactions via Environmental APT**, ***Krishna Rajan***, Iowa State University **INVITED**

In this presentation we describe the design and examples of applications of the use of an environmental cell integrated into a LEAP atom probe. The use of such a cell helps to open up the field of in-situ gas-solid reactions by permitting one to study surface and near surface reactions which are closer to ambient conditions than is possible in traditional surfaces science studies. The implications for this experimental approach in the context of the study of catalysts and nanomaterials are discussed.

3:00pm **AP+AS+EN+NS+SS-ThA3 Propagation of Chemical Waves: A Field Emission Microscopy Study**, ***Cédric Barroo***, *Y. De Decker, N. Kruse, T. Visart de Bocarmé*, Université Libre de Bruxelles, Belgium

Thecatalytic hydrogenation of NO_2 over platinum field emitter tips has been investigated by means of field emission techniques. Field emission microscopy (FEM), as well as field ion microscopy (FIM), has been proved to be an efficient method to study the dynamics of catalytic reactions occurring at the surface of a nanosized metal tip, which represents a good model of a single catalytic nanoparticle. These studies are performed during the ongoing reaction which is imaged in real time and space. Nanoscale resolution allows for a local indication of the instantaneous surface composition.

The presence of adsorbates modifies the value of the local work function. These variations are expressed by modulations of the brightness of field emission patterns. A qualitative investigation of the local surface composition is then possible as function of time.

The microscope is run as an open nanoreactor, ensuring that the system is kept far from thermodynamic equilibrium. Under these conditions, chemical reactions can induce time and space symmetry breaking of the composition of a system, for which periodic oscillations and target patterns are well-known examples.

Self-sustained periodic oscillations have been reported for the NO_2 reduction. By increasing the time resolution of the system, it is now possible to study the emergence of these oscillations and to observe the propagation of chemical waves at the nanoscale, on a single facet of a nanocrystal. The velocity of wave propagation is estimated to be in the μm/s range, which is in accordance with previous studies of catalytic reaction at the mesoscale.

3:20pm **AP+AS+EN+NS+SS-ThA4 3D Nanoscale Chemical/Structure Analysis in Mineral Carbon Sequestration Study using Atom Probe Tomography**, ***Jia Liu***, *D.E. Perea, R.J. Colby, L. Kovarik, B. Arey, O. Qafoku, A. Felmy*, Pacific Northwest National Laboratory

Mineral carbon sequestration is one of the important means to store CO_2 in order to mitigate the environmental concern regarding ever-growing anthropogenic CO_2 emissions. Olivines, X_2SiO_4 where X = Mg and Fe, hold promise as potential media to sequester carbon due to its broad availability in basalt deposits and reactivity to form stable metal carbonates. Site-specific reactivity of olivine with supercritical CO_2 is of great interest in understanding the fundamental elementary reaction mechanisms, where the presence of impurities within the bulk mineral may affect reaction kinetics. A combination of atom probe tomography (APT) and scanning transmission electron microscopy (STEM) is being used to map the complex composition and nanoscale structure across various site-specific regions. APT analysis of unreacted natural fayalite indicates the presence of 2-3-nm-thick hydrated iron oxide layers. In addition, Na impurities were found to concentrate within the hydrated layers while Mg and Mn were depleted from these regions. With the ability of APT to detect the chemical/structural heterogeneity at nanometer-scale, we find that APT will provide a means to correlate with ongoing experimental reaction studies and also provide guidance into models of the heterogeneous phase formation and reaction rates at precisely defined interfaces within minerals.

4:00pm **AP+AS+EN+NS+SS-ThA6 Catalyst Nanomaterials Analysis via Atom Probe Tomography**, *P.A.J. Bagot*, Oxford University, UK, *Q. Yang*, University of Oxford, UK, *K. Kruska*, Pacific Northwest National Laboratory, *D. Haley*, University of Oxford, UK, *E. Marceau, X. Carrier*, Université Pierre et Marie Curie, France, ***Michael Moody***, University of Oxford, UK **INVITED**

Heterogeneous catalytic materials play an increasingly critical, yet largely unnoticed, role underpinning countless modern technologies. Their active components are generally transition group metals, each of which offers different catalytic properties in terms of selectivity, yield and stability under demanding operating conditions. The need to develop more efficient catalysts that meet industrial demands and comply with environmental legislation targets requires better understanding how different catalysts may alter at the atomic scale in terms of structure or surface composition under their respective operating environments. Further, many catalysts take the form of nanoparticles, the performance of which can be strongly correlated to size, shape, chemistry and structure. However, discerning the nature of nanoparticles scale poses significant challenges to conventional microscopy.

Recently, atom probe tomography (APT) techniques have been developed to provide unique insight into the behaviour of catalyst alloys subject to conditions like those experienced in service [1–3]. This study is aimed at more accurate and insightful analyses comprising unique 3D atomistic descriptions of the evolving alloy nanostructure which can then be correlated to catalyst performance. Here, APT results are presented for characterization of oxidation-induced segregation in a Pt-Pd-Rh gauze and Fe-Ni alloy catalysts. Progress in the development of new approaches for the analysis of nanoparticles via APT is also presented.

[1] T. Li et al., Atomic engineering of platinum alloy surfaces. Ultramicroscopy 132, 205 (2013).

[2] T. Li et al., Atomic Imaging of Carbon-Supported Pt, Pt/Co, and Ir@Pt Nanocatalysts by Atom-Probe Tomography. ACS Catalysis 4, 695 (2014).

[3] P. Felfer et al, Long-Chain Terminal Alcohols through Catalytic CO Hydrogenation. Journal of the American Chemical Society 135, 7114 (2013).

Atom Probe Tomography Focus Topic
Room: Hall D - Session AP-ThP

Atom Probe Tomography Poster Session

AP-ThP1 Nanoscale Semiconductor and Oxide Characterization using Atom Probe Tomography, ***David Larson***, *M. Ulfig, D. Lenz, D. Lawrence, D. Olson, D.A. Reinhard, T.J. Prosa, P.H. Clifton, T.F. Kelly*, CAMECA Instruments Inc.

Atom probe tomography (APT) is being used for an ever widening range of applications [1-3] and is now used by the majority of the leading semiconductor manufactures around the world for research and development [4]. The recent adoption of APT in studying complex semiconductor devices is driven by a combination of the need for nanoscale 3D dopant characterization [5] as well as the concurrent advances in sample preparation methods and advanced control of commercial APT systems [3]. Recent years have seen continued improvements such as flexible data acquisition control, signal-to-noise ratio improvement, compositional accuracy, and yield through improved control of software and hardware.

Yield in APT is often a limitation in extending the technique to non-traditional, material systems. Advanced proportional, integral, differential (PID) control algorithms have been developed to allow stable data collection at lower rates with very fast response times. This feature enables data collection at more optimal conditions to promote higher yield. Additionally, in laser mode, keeping the focussed laser spot optimally aligned with specimen apex is critical to both yield and data quality. Adaptive scan and focus algorithms with smart PID control have been shown to be especially useful in low data collection rate modes to acheive improved yield and accommodate changing environmental conditions. Examples of these advances will be shown.

The nature of APT requires that the entire region of interest (ROI) be captured within a volume roughly 200nm on a side. As applications of APT have expanded, analyses are often limited by the capability to isolate a given region within the bounds of an APT sample geometry. Recently, preparation techniques which allow for re-orientation and isolation of highly discreet ROIs have been developed. These techniques use a focused ion beam system to create markers (in this case holes) in a sample which delineate a specific region. Using this method (known as “targeted backside preparation” [6]), the region of interest is subsequently positioned in a specimen apex in a reversed orientation. This method improves often yield in many difficult materials cases, such as single device analysis or failure analysis.

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

[2] E. A. Marquis *et al*, Current Opinions in Solid State and Materials Science 17 (2013) p. 217.

[3] D.J. Larson *et al*, “Local Electrode Atom Probe Tomography”, (Springer Science+Business Media,

New York) 2013.

[4] McClean Report, IC insights **17** (2013).

[5] http://public.itrs.net/ .

[6] D. Lawrence *et al*, 7th Annual FIB SEM Workshop (2014).

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+NS+SS-FrM

Correlative Surface and Interface Analysis with APT

Moderator: Arun Devaraj, Pacific Northwest National Laboratory

8:20am **AP+AS+NS+SS-FrM1 Correlative Transmission Electron Microscopy and Atom Probe Tomography of Interfaces in CdTe**, ***David Diercks***, *J.J. Li, C.A. Wolden, B.P. Gorman*, Colorado School of Mines **INVITED**

CdTe solar cells are a promising thin film technology, yet the highest reported efficiencies [1] remain well below the theoretical efficiency for such materials. For polycrystalline CdTe, interface contacts and grain boundaries along with impurities likely account for the majority of this underperformance.

Atomic scale analysis is an important feedback mechanism to relate the structure to both the device performance and the processing conditions. Through this, the atomic scale factors which improve or limit the performance can be ascertained. This then enables the development of materials and processing methods which best eliminate or mitigate the detrimental effects.

With these goals, atom probe tomography (APT) in conjunction with transmission electron microscopy (TEM) was used to study the contact interfaces and grain boundaries in CdTe devices. With the combination of time-of-flight mass spectrometry and point projection microscopy by controlled field evaporation, APT has the ability to obtain tens of ppm composition sensitivity along with near atomic-level spatial resolution. TEM provides crystallographic information along with other correlative information for guiding the reconstruction of the APT data.

It is demonstrated that the compositions measured for CdTe by APT are sensitive to the analysis conditions. Therefore, the APT analysis conditions for obtaining accurate measurements of the specimen stoichiometry were first ascertained. Following that, TEM and APT analyses of thin film devices consisting of a fluorine-doped tin oxide coated glass substrate subsequently coated with CdS, CdTe, Cu-doped ZnTe, and Au were performed. Using optimized values, APT analyses on the absorber layers and contact interfaces after different deposition and processing conditions were performed. These show significant changes in copper and sodium distributions as a result of the thermal processing.

[1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, "Solar cell efficiency tables (version 42)," *Progress in Photovoltaics,* vol. 21, pp. 827-837, Aug 2013.

9:00am **AP+AS+NS+SS-FrM3 Atom Probe Compositional Analysis of Nanoscale Precipitates in Nb-Ti Micro-alloyed Steels**, ***Monica Kapoor***, *G.B. Thompson,* University of Alabama, *R.M. O'Malley*, Nucor Steel

Composition of complex carbide and carbo-nitride precipitates in Ti-Nb micro-alloyed 80-ksi (0.06 wt. % Nb; 0.06 wt. % Ti) and 100-ksi (0.03 wt. % Nb; 0.12 wt. % Ti) steels was studied using atom probe tomography. Fine (~2 nm) and coarse (~8 nm) NbTiC precipitates were identified in the 100 ksi steel with the Fe content decreasing with increasing precipitate size. Both steels had coarse NbTiCN precipitates (~ 80 nm) having ~7 at. % and ~30 at. % Nb in the precipitates for the 100 ksi and 80 ksi steels respectively. Star-shaped TiC precipitates and parallel rows of interphase NbTiC clusters on and near grain boundaries were also identified in the 100 ksi steel. In the 80 ksi steels, uniformly distributed disk-shaped and spherical NbTiC clusters were observed along dislocations. The composition and phase stability of these precipitates are discussed in terms of Thermo-Calc solution thermodynamic modeling.

9:20am **AP+AS+NS+SS-FrM4 Nanoscale Imaging of Li and B in Glass Samples, a Comparison of ToF-SIMS, NanoSIMS, and APT**, ***Zihua Zhu***, *Z.Y. Wang, J. Liu, J. Crum, J.V. Ryan, D.K. Schreiber, J.J. Neeway*, Pacific Northwest National Laboratory

A widely used method to immobilize nuclear wastes is fusing them into glasses. These proposed glass waste forms are multicomponent complex material with the common components of Li and B compounds. It is difficult for commonly-used surface analysis tools (e.g., X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, scanning electron microscope/energy dispersive spectroscopy (SEM/EDX), and transmission electron microscope/energy dispersive spectroscopy (TEM/EDX)) to image the distributions of ultra-light elements like Li and B with sub-micron lateral resolutions. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), NanoSIMS, and atom probe topography (APT) were used to image Li and B distributions in several representative glass samples. ToF-SIMS can provide ~100 nm lateral resolutions if using Li^+ and BO_2^- images. However, both positive ion mode and negative ion mode are needed because neither B signals in positive ion mode nor Li signals in negative ion mode can provide adequate intensity to form qualified images. NanoSIMS can provide ~100 nm lateral resolutions if using Li^- and BO_2^- images, while the lateral resolution of positive ion mode of NanoSIMS is poor (~400 nm). APT can provide ~2 nm lateral resolution for Li^+ and B^+ in a 3-D mode and quantification of APT is better than that of SIMS. While APT can provide much better ultimate lateral resolution than ToF-SIMS and NanoSIMS, it has three drawbacks: limited field-of-view, time-consuming sample preparation, and frequent/unpredicted sample damage during measurement. As a comparison, field-of-view of SIMS is flexible, sample preparation is simple, and little unpredicted sample damage occurs during SIMS measurement. Therefore, SIMS and APT can be regarded as complimentary techniques in nanoscale imaging of Li and B in glass samples.

9:40am **AP+AS+NS+SS-FrM5 Application of (S)TEM and Related Techniques to Atom Probe Specimens**, ***William Lefebvre***, *D. Hernandez-Maldonado, F. Cuvilly, F. Moyon*, University of Rouen, France **INVITED**

The geometry of atom probe tomography (APT) specimens strongly differs from standard scanning transmission electron microscopy (STEM) foils. Whereas the later are rather flat and thin, APT tips display a curved surface and a significantly larger thickness. As far as a correlative approach aims at analysing the same specimen by STEM and APT, it is mandatory to explore the limits and advantages imposed by the particular geometry of APT specimens to STEM.

High angle annular dark field (HAADF) in STEM provides a contrast related to atomic number and to the amount of atoms in a column. A complete analysis of a high resolution HAADF STEM image requires the identification of projected column positions, the calculation of integrated HAADF intensity for each column and, eventually, the estimation of a "background level" generated by the amorphous carbon or oxide layer present on the specimen surface. Then, by of a statistical analysis [1], the possibility of atomic counting in an APT specimen can be explored. For this purpose, we propose an image processing method which provides a complete analysis of HAADF STEM images, that was applied here to APT specimens. In order to estimate the advantages and limitations of the method for such a particular specimen geometry, simulations have been applied and confronted to experimental results. Illustrations will be given for specimens before and after field evaporation in APT.

[1] S. Van Aert et al. Phys. Rev. B 87 (2013) 064107

10:40am **AP+AS+NS+SS-FrM8 APT Analysis of Biological Materials**, ***Daniel Perea***, *J. Liu, J.A. Bartrand, N.D. Browning, J.E. Evans*, Pacific Northwest National Laboratory **INVITED**

Biointerfaces play an essential role for the function of many biological materials and organisms. The behaviors of complex macromolecular systems at materials interfaces are important in the fields of biology, environmental biology, biotechnology, and medicine. An understanding of the chemical processes and physics, and ultimate the ability to engineer biomaterials and microorganisms with specific properties and functions, is aided by an atomic level understanding of the composition and morphology of biointerfaces. However, a great challenge exists to map the atomic level composition and morphology of biointerfaces using APT, precluding a complete understanding of the structure properties relationship. At the Environmental Molecular Sciences Laboratory (EMSL), the application of APT is being developed in combination with other microscopy and spectroscopic techniques to study interfaces in biologic materials. We are developing methodologies and analyses that are allowing us to probe the ultimate limits of what APT analysis can confidently provide despite the complex thermally-assisted field evaporation behavior of soft materials. Advanced sample preparation techniques will also be discussed that further advance the application of APT into field of biology.

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