

# Tuesday Afternoon, October 29, 2013

## Applied Surface Science

Room: 204 - Session AS+BI-TuA

### Forensic Science, Art and Archaeology (2:00-3:20 pm)/Quasicrystals and Complex Metal Alloys (4:00-6:00 pm)

**Moderator:** J.A. Ohlhausen, Sandia National Laboratories, R. Opila, University of Delaware, S.J. Pachuta, 3M Company

#### 2:00pm AS+BI-TuA1 Validation of Ultra-Trace Biological Agent Sample Matching Using NanoSIMS, P.K. Weber, M.L. Davisson, C.E. Ramon, S.P. Velsko, Lawrence Livermore National Laboratory INVITED

The threat associated with the potential use of radiological, nuclear, chemical and biological materials in terrorist acts has resulted in new fields of forensic science using state-of-the-science analytical techniques. One such method is high spatial resolution secondary ion mass spectrometry (SIMS) performed with a Cameca NanoSIMS 50. This instrument allows us to extract quantitative trace element and isotopic information for forensic purposes at a resolution of ~100 nanometers. With this capability, target particles with contaminated or ultra-trace samples can be analyzed. Here we present a general validation scheme and extend it to the analysis of small numbers (3-10) of anthrax spores. The scheme tests the hypothesis that two samples were produced in the same laboratory by the same process. This test is generally known as "sample matching", though the term "match" is not used. Instead, the test uses receiver-operating characteristics (ROC) curves derived from test samples to generate a likelihood ratio that is combined with other data relating to the hypothesis. For our work, we are using the elemental composition of single anthrax spores as evidence.

To evaluate the sample matching test we used a well-defined statistical design to generate *B. anthracis* samples that are representative of agents made by benchtop scale processes that might be encountered in terrorism events. We used the NanoSIMS to profile the elemental composition of individual bacterial spores. Between 8 and 20 elements were monitored. The dynamic range of the analyses was on the order of one million. An objective metric for the "closeness" of two samples was defined in terms of the differences between elemental concentrations. A ROC curve for the same lab-same process and same batch hypothesis tests were calculated based on the difference metric. The ROC curves for averages of small numbers of spores (3-10) were determined, and were compared to bulk elemental analysis.

Our results support the following conclusions: The average elemental composition of two samples containing a small number of spores (3 - 10) can have reasonable inferential power for determining if the samples were made in the same laboratory using the same process. The ROC curve for determining if two samples originate from the same batch offer less inferential power than those for the same lab - same process test. ROC curves for NanoSIMS-based comparisons are optimized by using a particular set of elements, but the dependence on element set is relatively weak.

#### 2:40pm AS+BI-TuA3 Characterization of Foreign Material from Buried Interfaces in the Medical Device Industry, W. Theilacker, A. Belu, A. Burand, Medtronic, Inc.

This presentation will highlight the use of surface analysis methods for the characterization of buried interfaces on medical devices. Manufacturing of medical devices requires the highest level of quality to ensure optimal device performance and patient safety. Pacemakers, leads, and cardiovascular products often contain components and sub-systems that are potted in an overlayer of semi-transparent material including silicones, urethanes, cyanoacrylates, and epoxies. This process serves to isolate electrical feedthroughs and contacts, fill gaps and voids, and to create water tight seals. Occasionally surface residues from raw materials, manufacturing processes, cleaning, and handling become trapped at this interface and are often not detected until later in the build process. Their presence could degrade performance, prevent adhesion, generate corrosion, or simply result in a cosmetic blemish. Identifying the elemental and chemical composition of foreign material from buried interfaces is a very difficult task and often requires a multi-technique approach. In this study, titanium, polycarbonate, and silicon-based substrates were coated with a thin layer of commonly observed inorganic and organic manufacturing residues and buried under overlayers (<100 nm) of various organic materials. Both non-destructive (e.g., confocal Raman spectroscopy) and destructive analysis (e.g., ion beam sputtering along with XPS and TOF-

SIMS) were applied to gain insight into the chemical composition of the interfacial regions.

#### 3:00pm AS+BI-TuA4 Forensic XPS Characterization of Surface-Modified Textile Fibers, B. Strohmaier, Thermo Fisher Scientific, C. Deeks, Thermo Fisher Scientific, UK, R. Blackledge, Forensic Chemist Consultant

Despite its many advantages and unique capabilities as a surface analytical technique, X-ray photoelectron spectroscopy (XPS) has not been widely used in forensic science for the examination of specimens gathered at the scene of a crime. Reasons for the lack of forensic XPS studies in the past include: 1) the absence of standard forensic XPS methods and standard reference materials for comparison to real world samples; and 2) the historical long analysis times (e.g., hours per sample), relatively large analysis areas (e.g., several square millimeters), and the relative high cost of XPS instrumentation compared to more common forensic analytical tools such as scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS), Fourier transform infrared (FT-IR) microscopy, and Raman microscopy. Advances in XPS instrumentation over the last few decades, however, have improved typical analysis times to minutes per sample and analysis areas down to the range of tens to hundreds of micrometers. In addition, recently developed argon cluster ion sources now allow depth profiling of organic species with minimal ion beam damage, thus preserving the chemical information available from XPS. Therefore, XPS has increased potential for new applications in forensic science. One such area is the forensic surface characterization of textile fibers. White cotton fibers are so common and have so few visual distinguishing features that they are largely ignored by forensic scientists at crime scenes. However, most fabrics today have received one or more types of organic-based surface-modification treatments to provide stain resistance, permanent press characteristics, and/or waterproof properties. This presentation will discuss a proof of concept study on the use of XPS to differentiate individual textile fibers based on their surface chemistry. Materials examined in this study included swatches, threads, and individual fibers from a variety of different cotton and polyester/rayon fabrics before and after receiving one of several different commercial textile surface-treatments. Results indicated that small spot XPS combined with argon cluster ion depth profiling can: 1) distinguish among various untreated textile materials based on differences in surface chemistry resulting from their specific manufacturing process; and 2) distinguish between otherwise identical appearing fibers by differences in the textile surface treatment applied. These results demonstrate that XPS has the potential for identifying and distinguishing textile fibers found at crime scenes.

#### 4:00pm AS+BI-TuA7 Surface Properties and Complexity of Al-based Intermetallics, J.-M. Dubois, CNRS, France INVITED

Quasicrystals represent the ultimate state of lattice complexity in a crystal. Shechtman, who discovered quasicrystals,<sup>1</sup> was awarded a Nobel Prize in Chemistry in 2011 for having led to a revolution in the way ordered solids are now understood in materials science. The talk will focus on a specific series of compounds, namely Al-based complex metallic alloys (CMAs) which comprise a significant number of crystalline compounds of changing lattice complexity, according to composition, and yield few icosahedral compounds that are thermodynamically stable and may be prepared into various sample shapes that allow for the measurement of surface physical properties.

Surface energy ( $\gamma_s$ ) is one of the few fundamental properties of condensed matter: it defines the equilibrium shape of a crystal, it determines the interfacial behavior of any piece of liquid or solid against another body, etc. The talk will summarize a number of attempts to estimate the surface energy of a large variety of CMAs, including the stable, icosahedral Al-Cu-Fe and Al-Pd-Mn quasicrystals.

Pin-on-disk experiments, after appropriate calibration, lead to reliable data that fall in the range  $0.5 < \gamma_s < 0.8 \text{ Jm}^{-2}$  for these compounds.<sup>2</sup> The average value of  $\gamma_s$  is about one half that of pure aluminum ( $\gamma_s = 1.15\text{-}1.2 \text{ Jm}^{-2}$ ), and less than a quarter that of iron ( $\gamma_s = 2.2\text{-}2.4 \text{ Jm}^{-2}$ ). It is consistent with the low wetting behavior and reduced adhesion force against hard steel observed in high vacuum for these quasicrystals. Correlation to specific features of the electronic density of states will be emphasized, in line with the varying complexity of the studied CMA compounds. Potential applications in high vacuum technology will be addressed.

References:

- 1- D. Shechtman, I. Blech, D. Gratias and J.W. Cahn, Phys. Rev. Lett., 1984, **53-20**, 1951.
- 2- E. Belin-Ferré and J.M. Dubois, Int. J. Mat. Res., **97** (2006) 7.

4:40pm **AS+BI-TuA9 Structural Investigation of the (001) Surface of  $\text{Al}_5\text{Co}_2$** , M. Meier, J. Ledieu, M.-C. de Weerd, E. Gaudry, V. Fournée, CNRS-Université de Lorraine, France

Complex metallic alloys (CMAs) like quasicrystals and approximants are being considered as low-cost alternative materials for heterogeneous catalysis [1,2]. It relies on the so-called site-isolation concept in which the catalytic performance of a material is ascribed to small and well-separated atomic ensembles containing an active transition metal (TM) element at the crystal surface. Such atomic ensembles must be stable under reaction conditions, which in turn depend on the chemical bonding and the crystal structure of the intermetallic compound.  $\text{Al}_{13}\text{TM}_4$  compounds have been identified as promising candidates for the heterogeneous hydrogenation catalysis [2, 3]. Here we focus on a related CMA system, the  $\text{Al}_5\text{Co}_2$  crystal, which is also considered as a quasicrystalline approximant.

As a first step towards the understanding of the catalytic properties of this new phase, an atomic scale description of its surface is mandatory. First, a single crystal has been grown using the Czochralski method and oriented perpendicular to its [001] axis. The surface structure investigated under ultrahigh vacuum conditions by low energy electron diffraction and scanning tunnelling microscopy (STM) exhibits a  $\sqrt{3}\times\sqrt{3}R30^\circ$  reconstruction. According to the bulk model, two types of atomic layers are stacked along the [001] direction: either pure Al puckered (P) layers or flat (F) layers containing both Al and Co atoms. The step height measured by STM indicates that only one type of plane appears as surface termination. Atomically resolved STM images show small triangular atomic ensembles separated by 13 Å from each other and consisting of 3 bright protrusions. Such local configurations can only be interpreted as a reconstructed P layer where a fraction of Al atoms are missing. First-principles calculations using density functional theory (DFT) confirm that P layers are preferred terminations compared to F layers. Calculated surface energies for various surface models, along with the corresponding simulated STM images, show that the  $\sqrt{3}\times\sqrt{3}R30^\circ$  reconstruction is due to a specific set of missing Al surface atoms. Finally, a very nice agreement is obtained between simulated and experimental STM images, thus confirming the surface model. Other surfaces of interest for catalysis are currently being studied, namely the (100) and the (2-10) surfaces, together with their chemical reactivity towards small molecules of interest ( $\text{O}_2$ , CO, acetylene,...).

[1] T. Tanabe, S. Kameoka, A. P. Tsai, *Appl. Catal.*, A 384, 241 (2010).

[2] M. Armbrüster, K. Kovnir, M. Friedrich, *et al.* *Nat. Mater.* 11, 690 (2012).

[3] J. Ledieu, É. Gaudry, L. N. Serkovic Loli, *et al.* *Phys. Rev. Lett.* 110, 076102 (2013).

5:00pm **AS+BI-TuA10 Temperature-Dependence of Ag Film Roughness and Interlayer Spacings During Deposition on Complex Al-Pd-Mn Surfaces: Comparison with Periodic Substrates**, B. Únal, Massachusetts Institute of Technology, J.W. Evans, P.A. Thiel, Ames Laboratory and Iowa State University

The morphology of thin metal films deposited on metal substrates is often dominated by kinetic rather than thermodynamic factors. These factors can be assessed by studying film characteristics as a function of deposition temperature. In this study, we report a comparison of the roughness of thin Ag films deposited on surfaces of a quasicrystal (five-fold icosahedral Al-Pd-Mn), an approximant of this quasicrystal, and low-index Ag surfaces, at temperatures below and up to ambient. Kinetic effects lead to an increase in roughness with increasing temperature for the Al-Pd-Mn substrates, but a decrease in roughness over the same range on Ag(111) and Ag(100). The nature of these effects is discussed. In addition, we observe that interlayer spacings in the film depend upon layer height, for the Al-Pd-Mn substrates. A useful refined definition of roughness for a system with variable interlayer spacing is addressed.

5:20pm **AS+BI-TuA11 Study of Quasicrystal /  $\alpha$  - Mg Eutectic Structure in the Mg-Cd-Yb System by EBSD**, A.P. Tsai, Tohoku University, Japan

A pseudo-binary phase diagram composed of iQc (icosahedral quasicrystal) and  $\alpha$ -Mg in Mg-Cd-Yb system reveals a eutectic reaction at  $\text{Mg}_{68}\text{Cd}_{24}\text{Yb}_8$ . The alloy with eutectic composition prepared by slow cooling shows irregular eutectic structure of QC and  $\alpha$  phases. In terms of interface stability, the iQc /  $\alpha$  interfaces are realized to be most stable since eutectic structure contains largest area of interface. This study is aiming at understanding an essential question; “how does a quasiperiodic lattice match a periodic lattice?” The other challenging topic is the application of EBSD (Electron Back Scattering Diffraction) for the first time to study microstructure of a quasicrystalline material.

In X-ray diffraction patterns, a number of main peaks of iQc coincide with those of  $\alpha$  phase, indicating good lattice matches between two phases. For examples, basal plane and prismatic plane of  $\alpha$  phase have the similar lattice

spacing to 2-fold symmetry plane and 5-fold symmetry plane, respectively. EBSD analysis revealed that the growth direction of iQc- $\alpha$  eutectic is  $_{,2f} \cdot$  iQc.  $//_{,1} 0_{,1} 0_{,1} \cdot$  Mg. and a number of orientation relationships between QC and  $\alpha$  phase have been verified. Furthermore, a number of directions normal to the planes of iQc coincide to those normal to the planes having similar lattice spacing of iQc in the  $\alpha$  phase. The interface stability is likely due to good lattice matches between iQc and  $\alpha$  phase.

5:40pm **AS+BI-TuA12 Plasmonic Quasicrystal Lattices**, T.W. Odom, Northwestern University

Quasicrystals are ordered materials that do not have translational symmetry but form stable structures with rotational symmetries higher than periodic materials. Artificially structured high-symmetry lattices based on quasicrystalline structures have recently been generated using nanoparticle building blocks and nanoholes. The design of quasicrystal arrays with subwavelength spacings is especially important in photonics since such symmetries can result in full band gaps in photonic crystals and omnidirectionally trap light in patterned photovoltaic devices. This talk will describe a novel nanofabrication method—moiré nanolithography—that can fabricate subwavelength lattices with high rotational symmetries over wafer-scale areas. By exposing elastomeric photomasks sequentially at multiple offset angles, we could create nanoscale arrays with rotational symmetries as high as 36-fold, which is three times higher than quasiperiodic lattices ( $\leq 12$ -fold) and six times higher than two-dimensional periodic lattices ( $\leq 6$ -fold). We transferred these patterns into noble metal films to generate plasmonic quasicrystal lattices, which show unique optical properties. A new scheme required for indexing these new plasmonic modes will be discussed.

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