Friday Morning, November 14, 2014

Applied Surface Science
Room: 316 - Session AS+MC+SS-FrM

Practical Surface Analysis II
Moderator: Steven Pachuta, 3M Company

8:20am AS+MC+SS-FrM1 Vector Potential Photoelectron Microscopy, *Raymond Browning*, R. Browning Consultants
Vector potential photoelectron microscopy (VPPEM) is a new class of synchrotron based analytic spectromicroscopy using NEXAFS and XPS spectroscopy. To optimize the spatial resolution VPPEM images very low energy photoelectrons which poses both challenges and opportunities. At low energies the NEXAFS signals have an information depth that is similar to that from total yield absorption (TAY) measurements, while the XPS signals have a variable information depth from the universal curve at low energies. VPPEM has a very high depth of focus, and immunity to many imaging artifacts such as surface charging, and magnetic state. This makes VPPEM suitable for analyzing real world samples, and we present some results from the prototype instrument at NSLS.

8:40am AS+MC+SS-FrM2 Hydrogen and Chemical Quantification of an Organic Coating, *Paul Mack*, Thermo Fisher Scientific, UK
Zinc-coated steel substrates often have an additional organic coating applied, protecting the steel surface or altering its appearance for decorative reasons. X-ray Photoelectron Spectroscopy (XPS) is an analysis technique which provides chemical bonding information from the top few nanometres of a surface down to many microns in depth. It is the ideal technique, for example, for identifying the carbon functional groups in these organic coatings. XPS cannot detect hydrogen, however, but the complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) is able to both detect and quantify hydrogen. REELS can also be used to discern between aliphatic and aromatic carbon in the organic coatings.

There is also a requirement for compositional profiling of these coatings, combining the excellent depth resolution and chemical specificity of XPS with some kind of ion beam sputtering. Traditional methods such as argon monomer ion profiling can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials. Numerous studies over recent years, however, has shown that argon cluster beams may be used for depth profiling while preserving chemical information during analysis of organic materials.

This talk will present data from cluster profiling studies of an organic coating on steel. The data will be compared with an alternative method of profiling the coating, i.e. ultra low angle microtomy. A complete elemental compositional profile of the coating, including hydrogen, will be presented.

9:00am AS+MC+SS-FrM3 Mechanical Strain Induced Tunable Reflective and Conducting Silver Nanorods Embedded PDMS Film, *Pratibha Goel*, J.P. Singh*, Indian Institute of Technology, India
The formation of metallic films on both inorganic and organic polymeric substrate continues to be of substantial interest because of various applications.[1,2] Polymeric supports offer the obvious advantages in weight, flexibility, elasticity, and fragile relative to inorganic support such as glasses, ceramics, or native metal. Silver is a metal of choice as a reflecting material because of its high reflection coefficient (0.93). Silver also has the highest electrical conductivity of all metals at 6.3×10^7 $(\Omega m)^{-1}$. However, there are disadvantages of using silver as the reflecting metal. Firstly, silver is a relatively soft metal so that the face of a mirror needs to be carefully protected from mechanical abrasion. Secondly, silver tends to tarnish which diminishes its reflectivity. (Ambient sulfur-containing compounds are a particular problem.) Thirdly, and perhaps the most important, silver(0), as a more passive metal, does not interact strongly with organic functionalities, which means that adhesion of a silver layer on a polymer surface can be a substantial problem.

In this study we present a straightforward two step fabrication of highly adherent, reflective and surface conductive flexible films. First, the Ag nanorods were deposited on the Si (001) substrates by thermal evaporation of silver powder using oblique angle deposition (OAD).[3] Then the thermal curing of the PDMS on the Ag nanorods grown Si wafer leads to the copolymerization yielding a flexible, reflective and conductive silver surface approaching that of the native film. The Fig. 1 shows schematically the route followed for the fabrication of the sample. As prepared sample appear to be highly reflecting and conducting with the reflectance (R) of 64.17 % at 530 nm and sheet resistance (R_s) of 24.03 Ω/sq. Elongation of the sample up to 30% of its original length results into decrease in the reflectance and increase in R_s. Fig. 2 shows the tunability of the R at 531 nm and R_s with respect to the strain applied. Adhesion between the silver nanorods and the polymeric PDMS film was outstanding. No adhesive tapes removed any silver from the surface. Our sample may find potential applications in multifunctional devices where tunability of reflectance and conductivity is desirable through flexibility.

References: 1. N. Hubin, L. Noethe, Science 262 (1993), 1390.

2. L. Yan, X. M. Zhao, G. M. Whitesides, J. Am. Chem. Soc. 120 (1998), 6179.

3. P. Goel, K. Singh, J. P. Singh, RSC Advances 4 (2014),11130.

9:40am AS+MC+SS-FrM5 Surface Analysis of Electronic Materials, *R.L. Opila, Kevin Jones, J. Church,* University of Delaware, *R. Gupta, V. Pallem, B. Lefevre,* Air Liquide, *X. Lin*, University of Delaware
Surface analysts at the University of Delaware have used a variety of surface analytical techniques to analyze films for electronic materials applications. These films were deposited by a variety of technique including plasma enhanced chemical vapor deposition, molecular organic chemical vapor deposition and atomic layer deposition using precursors synthesized at Air Liquide. Methods of analysis include x-ray photoelectron spectroscopy, scanning Auger electron spectroscopy, time-of-flight secondary ion spectrometry, nano-indentation and synchrotron-based hard x-ray analysis. The advantages of each technique for particular analyses will be discussed.

10:40am AS+MC+SS-FrM8 Lewis Base Sites on the Nitrogen-Doped Graphite Surfaces Probed by CO_2 Adsorption, *Takahiro Kondo, R. Shibuya, S. Morohoshi, D. Guo, J. Nakamura*, University of Tsukuba, Japan
Carbon materials have been reported to exhibit unique adsorption property and catalytic activity when they have received specific treatments such as nitrogen doping. For example nitrogen-doped graphene has been reported to show the superior catalytic activity for the oxygen reduction reaction (ORR) in fuel cell [1]. To understand the origin of such specific properties at the atomic scale, we are now trying to examine the relationship among the localized electronic states of the carbon atoms, the adsorption property of the molecule, and the catalytic activity towards ORR by using model catalyst of graphite with surface science techniques. Previously, we have reported based on the scanning tunneling spectroscopy (STS) that the carbon atoms around a pyridinic-nitrogen (N having two N-C bonds) in a highly oriented pyrolytic graphite (HOPG) have occupied localized states near the Fermi level [2]. We consider that such carbon atoms may act as Lewis base sites [2] and may relate to the ORR activity. In this work, we have examined this hypothesis by observing the carbon dioxide adsorption property with temperature programmed desorption (TPD), ORR catalytic activity measurement, and X-ray photoelectron spectroscopy (XPS).

To prepare the pyridinic-nitrogen-doped graphite (pN-HOPG) as the model catalyst, we have firstly cleaved the HOPG at atmosphere and then bombarded it by the nitrogen ion through Ni patterned mask to make edges with N-termination. After the bombardment, the sample was put into HNO_3 solution for 72 hours to remove Ni impurity. The sample was annealed at 900 K for 2 hours in ultrahigh vacuum. XPS spectrum shows that the nitrogen in the prepared sample consists of over 60 % pyridinic-nitrogen, suggesting that nitrogen atoms are dominantly doped at the edges.

In TPD measurements, CO_2 desorption peak was observed at around 370 K from pN-HOPG after the 1000 L CO_2 exposure at 300 K, while no CO_2 desorption peak was observed from clean HOPG. These results indicate that Lewis base sites are formed on pN-HOPG. The same CO_2-TPD results were reproducibly observed by sequential 4 time measurements. This means Lewis base sites on pN-HOPG does not change by the CO_2 adsorption and desorption. Details of CO_2 adsorption properties on pN-HOPG, the relationship with ORR activity and the influence of nitrogen configuration on the carbon atoms in pN-HOPG will be discussed.

[1] L. Qu et al., ACS Nano, 4 (2010) 1321.

[2] T. Kondo, S. Casolo, T. Suzuki, T. Shikano, M. Sakurai, Y. Harada, M. Saito, M. Oshima, M. Trioni, G. Tantardini and J. Nakamura, Phys. Rev. B 86 (2012) 035436.

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* ASSD Student Award Finalist

11:00am **AS+MC+SS-FrM9** **Towards Spin-FETs: Growth and Characterization of Magnetoelectric Chromium Oxide Films on Graphene**, *Sean Stuart, E. Sachet, J.-P. Maria, J.E. Rowe, D.B. Dougherty,* North Carolina State University*, M. Ulrich,* Army Research Office

Graphene has brought spintronic devices that depend on the ability to transport spin much

closer to realization. Graphene's high carrier mobility and low spin-orbit scattering allow for efficient

spin transport, which has been demonstrated by several publications over useful length scales [1,2].

Further progress toward more sophisticated spintronic devices requires controllable manipulation of

spin polarized charge carriers. A graphene Spin-Field Effect Transistor has been proposed by

Semenov et al [3] that manipulates the spin of charge carriers in a graphene channel by an exchange

interaction with a hypothetical ferromagnetic dielectric. As an alternative that also adds functionality,

we have identified Cr2O3 as a material whose magnetoelectric properties would enable voltage

controlled switching of the exchange interaction. The Magnetoelectric properties of Cr2O3 have been

extensively studied [4], including recent reports of a robust electrically switched magnetic surface

state [5,6].

We used pulsed laser deposition to grow thin Cr2O3 films directly on HOPG. AFM shows a

smooth Cr2O3 film with the hopg topography preserved. X-Ray Diffraction shows that the film has a

(0001) texture for films grown at 300 - 650ºC, which is the strongest orientation of the

magnetoelectric effect. The magnetic polarization of the film can be aligned by magnetoelectric

annealing and locally switched with conducting AFM, the effects of both are observed by magnetic

force microscopy.

[1]. Han, et. Al. J. Mag & Mag. Mat. Vol. 234, Issue 4, (2012)

[2]. Bruno Dlubak, et al. Nat. phys, 8, 557 (2012)

[3]. Y. G. Semenov, et al. Appl. Phys. Lett. 91, 153105 (2007).

[4]. Manfred Fiebig Phys. D: Appl. Phys. 38 R123 (2005)

[5]. X. He, et al. Nat. Mater. 9, 579 (2010).

[6]. N. Wu, et. al., Phys. Rev. Lett. 106, 17 (2011).

11:20am **AS+MC+SS-FrM10** **Energy Loss Of Highly Charged Ions Implanted In MOS Dielectric Films**, *Radhey Shyam, D.D. Kulkarni, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik,* Clemson University

Energy loss measurements of highly charged ions in the low kinetic energy regime have been made using as-grown SiO_2 (170nm) targets. Highly charged Ar^{+Q} ions (Q=4, 8 and 11) with a kinetic energy of 1 keV were used to produced electronic excitations in the oxides. The irradiated regions of the oxide were then encapsulated under a top metallic contact to form metal-oxide-semiconductor (MOS) devices. The devices were probed with capacitance-voltage (C-V) measurements and the extracted flatband voltages from the C-V curves were correlated with ion energy (kinetic and potential).

The C-V results for highly charged ion experiments reveal that the changes in the flatband voltage and slope for implanted devices relative to the pristine devices can be used to delineate effects due to implanted ions only and ion induced damage. The results confirm that dose as well as and charge-dependent effects can be recorded for irradiation of oxides using this method. In particular, the results as a function of charge state indicate that there is a significant enhancement in the induced flatband voltage shift as the charge state of the beam is increased. This was quantified by measuring the flatband voltage shift across multiple ion doses for fixed incident charge states to obtain a normalized value of the shift induced per incident ion. These normalized results show an enhancement in the shift, which grows monotonically across our charge state data, from 1.14×10^{-12} V/ion for Ar^{1+} ions to 1.12×10^{-11} V/ion for Ar^{11+} ions. This enhancement in the shift is consistent with the increased potential energy of the higher charge states (e.g. 15 eV for Ar^{1+} and 2004 eV for Ar^{11+}). Viewed as a function of the ion charge state, these data suggest a near-quadratic dependence on the incident charge which is consistent with some theoretical predictions.

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