Surface Science
Room 104D - Session SS+2D-WeM
Synthesis, Characterization, and Surface Science of Novel Materials and Interfaces

Moderator: Talat Rahman, University of Central Florida

8:00am **SS+2D-WeM1 Early Stages of the Thermal-Induced Mobility of Ag in SiC***, **Daniel Velázquez**, R. Seibert, J. Terry,* Illinois Institute of Technology

Tri-structural isotropic (TRISO) particles are the fuel of choice for very-high temperature reactor technology. At the core, these spherical particles consist of an inner fuel kernel of UO2, UC2 or a combination of both, which is coated radially outward by successive layers of low density pyrolytic graphite, an inner high density pyrolytic graphite layer, silicon carbide (SiC) and an outer high density pyrolytic graphite layer. SiC is the main diffusion barrier against the release of fission products due to its hardness and high melting point. Nonetheless, irradiation testing of TRISO particles indicates that trace amounts of metallic fission products, such as Ag (which as a ~41 day half-life), diffuse through SiC. Competing theoretical and experimental observations that indicate that Ag diffuses through the bulk and through grain boundaries. Diffusion through grain boundaries is usually amplified due to the formation of large grains upon crystallization by heating. This leads to the formation of triangular micro pits in thin films, suggesting that a 3D version of this form of crystallization could facilitate even more the release of Ag. Previously XAFS and XPS have shown that Ag remains metallic in a SiC matrix, indicating that bulk diffusion is perhaps interstitial rather than substitutional. In this work we discuss the mobility of Ag films enclosedon layers of 3C-SiC by analyzing SEM images taken before and after annealing. Image analysis supported by surface spectroscopic and crystallographic techniques are used in order to estimate the release of Ag through SiC for Ag interlayers at various thicknesses and annealing temperatures. Preliminary analysis by SEM/EDS show that upon annealing Ag escapes through the SiC surface by three different mechanisms, which roughly in chronological are: 1) escape through triangular pits and grain boundaries in SiC; 2) agglomeration and formation ofsub-surface blisters which eventually rupture; 3) diffusion through the bulk of SiC when the trapped amounts of Ag are insufficient to form large blisters. During the third mechanism, we still observed sub-surface mobility in the form of dendritic paths. When the starting amount of Ag is reduced sub-surface diffusion is limited and the release of Ag is dominated by the escape through the triangular pits of SiC and bulk diffusion.

8:20am **SS+2D-WeM2 Quantitative Chemical State base on XPS Energy Scan Image Applied to Ni Fe corroded Samples***, **Vincent Fernandez**, J. Keraudy,* Université de Nantes, France*; N. Fairley,* Casa Software Ltd, UK*; P.Y. Jouan,* Université de Nantes, France

1. Introduction

Corrosion is a natural phenomenon where metals have a tendency to revert back to their natural, lower energy state. During many years, the most effective corrosion protection systems were based on the use of chromate-rich surface treatments. However, recently, the legislation imposed by the european commission, REACH (Registration, Evaluation, Authorization and Restrictions of Chemicals) prohibited the use of hexavalent chromium. Many alternatives have been explored so far, including the protection with monolayer and/or multilayers of thin films (Cr, CrN, Ti, TiN, NbN) deposited by magnetron sputtering process. Corrosion is a physical-chemical interaction between the metal and its environment. Most hard coatings (TiN, CrN, NbN) possess an higher corrosion resistance than less noble materials like steel, Al or Mg alloys. When the coatings are deposited on such less noble substrates and exposed to a corrosive atmosphere (ex : NaCl), the coated parts suffer from serious corrosive attack (pitting corrosion) due to inherent coating defects or inhomogeneities . This kind of corrosion is localized to the defect area and is characterized by the anodic dissolution of the substrate material with a high anodic current density at the defect site. It is generally called galvanic corrosion. In this study, Nickel thin film (2 micrometers) was deposited on steel substrate (XC38) using Direct Current Magnetron Sputtering from a Ni target. In order to simulate the corrosive attack, the coated part was exposed to a corrosive medium, i.e salt spray test. The test was conducted under continuous spray (24 hours) conditions (5wt.% NaCl) at a temperature of 35 °C according to the ASTM B117 standard procedure.

The morphology and the chemical environment of the corrosion products were analyzed respectively by optical microscopy and XPS investigations.

2. Results

The samples have conducting and isolating regions to avoid spatial differential potential the samples were measured in a floating condition. The Parallel XPS images of 128 pixels by 128 pixels where done with FOV of 900 x 900 microns at an energy resolution of about 1eV and an energy step of 0.2 eV for O 1s, Na KLL, Ca 2p, C 1s, Ni 3p and Fe 3p with charge compensation. Ni and Fe were measure in one region. To treat the 735 images corresponding of more than 1.2 10^7 intensity points, images were smoothed and projected on PCA images. All images were projected on 6 abstract factors. Then images were converting in 81920 spectra. After spectra quantification, energies regions were converting back in quantitative images. Then Fe map was classified in 5 false colors part by intensity.

8:40am **SS+2D-WeM3 Novel Approaches to Form Organic-Inorganic Interfaces: Parallels between Coupling and Surface Modification Schemes in Vacuum and in Wet Chemistry***, **Andrew Teplyakov**,* University of Delaware

Recent interest towards controlled formation of organic-inorganic interfaces affected greatly the approaches used for surface modification of semiconductors. Despite substantial progress in designing chemical pathways for surface modification of these materials and synthetic capabilities to build a variety of precursor molecules, two major issues remain: 1) Can the same level of precision achieved for surface characterization in vacuum be achieved for surfaces modified by wet chemistry methods; and 2) Can the elemental and compound semiconductor surfaces be modified with chemical groups that are both oxygen- and carbon-free. These two questions will be addressed by drawing parallels between cyclocondensation processes on modified semiconductor surfaces and cycloaddition in vacuum. Mixed surface modification schemes will be discussed for silicon and ZnO materials to produce high-coverage chemical “hooks” and the use of these functionalities will be demonstrated for initial stages of film deposition or depositing large constructs (nanoparticles and buckyballs) by chemical addition to produce strong covalent bonds. The addition across double bonds of carbonaceous constructs and the production of chemical bonds by straightforward chemical reactions will be discussed. The reactions for producing amino-functionalities and the platforms for “click” reactions will be presented. The experimental evidence of the reactions will be based on infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a combination of microscopic techniques. The selected results of the experimental work will be compared with the experimental observables predicted by density functional theory (DFT).

9:00am **SS+2D-WeM4 Adsorption of Hetero-bifunctional Urea on Ge(100)-2x1 Surface***, **Tania Sandoval**, S.F. Bent, A.M. Crow,* Stanford University

Organic functionalization of Group IV semiconductor surfaces is of interest due to the need for new pathways in surface chemistry modification. This is important in applications such as molecular layer deposition, molecular electronics, and biosensors where the ability to control and tune surface properties requires a deep understanding of the interactions between molecules and solid surfaces. In this study, adsorption of the heterobifunctional urea molecule on the Ge(100)-2x1 surface was investigated. Both the amine and carbonyl group of the urea molecule are known to react with the Ge surface. The aim of this study is to determine if any preferential reaction pathways exist and to understand the driving forces toward the final products.

Density functional theory (DFT) calculations suggest that NH_2 dissociation is the most thermodynamically favorable pathway for the single reaction. The reaction can occur through two possible precursor states: a nitrogen dative bond with the surface or an oxygen dative bond that can further undergo an enolization reaction. Interestingly, the oxygen dative bond is 7 kcal/mol more stable than the nitrogen bond, suggesting a preference for the latter reaction pathway. Furthermore, calculations show that the dual reactions provide less stabilization gain and a higher kinetic cost than single reactions, as the dual NH_2 dissociation has an activation barrier greater than 30 kcal/mol and only provides 5 kcal/mol of additional exothermicity, indicating that the urea molecule will likely react only through a single functional group. X-ray photoelectron spectroscopy (XPS) and multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy were used to determine the final reaction products. Results suggest that urea adsorbs on Ge(100) forming a mix of surface products. One of the products can be identified by the downshift in binding energy of the N(1s) XP peak and the Ge-H stretching mode in IR as NH_2-dissociated urea on Ge. This assignment is also consistent with the presence of a carbonyl group in the IR and XPS spectra, which is expected to remain unchanged in this surface configuration. Another reaction product exists that is evident by second O(1s) and C(1s) XPS peaks downshifted from that of the parent urea molecule, suggesting a loss of the carbonyl group by a reaction with a more electropositive atom. Moreover, coverage results support our DFT findings by suggesting that each urea molecule will occupy a Ge dimer by reacting through a single functional group per molecule.

9:20am **SS+2D-WeM5 Electronic Structure of Ferroelectric Nanodomains***,* ***Erie Morales****, C. Perez, M. Brukman, D. Bonnell,* The University of Pennsylvania

The local measurement of structure and properties enabled by scanning tunneling microscopy and atomic force microscopy in conjunction with systematic control of in situ environments has yielded insight into the fundamental behavior of ferroelectric compounds. Many atomic structures on BaTiO3 surfaces have been determined, the thermodynamic stability of structures on (001) surfaces has been described, and the polarization dependence of several classes of surfaces reactions has been demonstrated. In addition the polarization behavior at the nanoscale has received much attention.

Here we report unusual impact of local poling on the electronic structure of ferroelectric surfaces. Scanning Tunneling Microscopy in situ poling was performed on BaTiO3 (001) in ultra high vacuum (UHV). The voltage pulse produces apparent anti-parallel ferroelectric domains. Domain size can be controlled by changing conductivity of the crystal and/or by changing the bias set point; the smallest domain we pole is 24 nm. We use a 4-D analysis of geometric and electronic structure data to characterize the variations in electronic structure. Patterns of variations in the surface band gap are consistent with existing theoretical calculations of anti parallel domain orientations.

9:40am **SS+2D-WeM6 Using Data Analytics and Informatics in Understanding Enhanced Conductivity, Mobility, and Transparency in ITO Bearing ZrO_2 and reduced SnO_2***,* ***Timothy Peshek****,* Case Western Reserve University*; J.M. Burst, T. Coutts, T.A. Gessert,* National Renewable Energy Laboratory

We deposited high quality tin-oxide-doped indium oxide (ITO) by RF magnetron sputtering with varying oxygen partial pressure in the sputter ambient and using targets with a nominal concentration of 5 wt% SnO_2, instead of a typical 10 wt%, and between 0-3 wt% ZrO_2. We demonstrate mobilities of $>$45 cm^2/Vs for sputtered ITO films at zero added oxygen. We demonstrate resistivities in the range of 10^{-5} Ω-cm at zero added oxygen with 1 wt% ZrO_2 added, mobilities at >55 cm^2/Vs and the films showed a modest increase in optical transmission with increasing Zr-content.orptio

Hypothetically the increase in mobility that apparently accompanies the addition of ZrO_2 yields enhanced optical clarity in the IR due to reduced free carrier absorption from reduced doping concentration for any given resistivity.

Anomalous behavior was discovered for films with no Zr-added, where a bimodality of high and low mobilities were discovered for nominally similar growth conditions. We examined this anomalous behavior using modern data science and visualization techniques of big data and materials informatics. We used these techniques to gain insights into the mechanistic behavior of the relationship between stoichiometry, process variables, material morphology and electrical properties. We will summarize these findings and describe the methods used in the analysis and a path forward for continuing utilizing data analytics in material characterization and learning.

11:00am **SS+2D-WeM10 Surface Composition and Atomic Structure of Topological Insulator Materials***,* ***Jory Yarmoff****, W. Zhou, H. Zhu,* University of California - Riverside **INVITED**

A topological insulator (TI) is a two-dimensional material that behaves as an insulator in the bulk, but conducts along the surface via topologically protected surface states. TI's have attracted intense interest because of their fundamental importance combined with great potential for applications in areas such as spintronics and quantum computation. Because the critical electronic states in TI's are localized in the near-surface region, it is critical to understand their surface composition, surface atomic structure and surface chemistry, and there are several outstanding issues that have not been fully resolved. For example, the materials are often naturally doped leading to the Fermi energy residing in the conduction band. Some materials have also been observed to change over time, the so-called "aging effect". In addition, the surface termination of the prototypical TI, Bismuth Selenide (Bi_2Se_3), has been an area of recent debate. Although some studies have demonstrated that the cleaved surface is terminated with Se, as expected from the bulk crystal structure, there are other reports that show either a Bi-rich or mixed-termination.

We are using low energy ion scattering (LEIS), in conjunction with other surface analysis tools, to investigate the surface composition and atomic structure of TI materials prepared in numerous ways. LEIS is uniquely suited to measure surface termination and atomic structure, as it provides the elemental identification of the near-surface region and can be deployed to probe only the outermost atomic layer. We compared surfaces prepared by *ex situ* cleaving, *in situ* cleaving and Ar$^+$ ion bombardment and annealing (IBA) in ultra-high vacuum. LEIS measurements do not indicate any substantial differences between the Se-terminated surfaces prepared by IBA or *in-situ* cleaving. Samples inserted into the vacuum chamber following *ex-situ* cleaving are less well-ordered, show adsorbed oxygen and can be either Se-terminated or Bi-rich, which suggests a critical dependence on the level of contamination. We have also used molecular beam epitaxy to investigate the structure and stability of Bi overlayers grown on Bi_2Se_3. Additional experiments involve exposure of clean surfaces to gaseous species such as O_2, H_2 and Br_2.

11:40am **SS+2D-WeM12 Impact Collision Ion Scattering Spectroscopy of Bi_2Se_3 and Bi/Bi_2Se_3***,* ***Weimin Zhou****, H. Zhu, J.A. Yarmoff,* University of California - Riverside

Bismuth selenide (Bi_2Se_3) and isolated bilayers of bismuth both behave as topological insulators, which are two-dimensional materials that conduct along the surface through topological surface states (TSS). These materials show great promise for use in spintronics and quantum computation. Because the TSS are located at the surface, it is important to understand the relationships between the surface atomic and electronic structures. Low energy ion scattering (LEIS) is a simple, but powerful surface sensitive technique that is ideal for structural analysis. LEIS, using Na$^+$ projectiles, is employed here in two distinct modes. First, time-of-flight (TOF) spectra are collected using low index incidence directions. This allows for a direct measure of the surface termination with minimal beam damage. Second, impact collision ion scattering spectroscopy (ICISS), which involves the collection of angular distributions using a large scattering angle, is employed to study the structure of the outermost few atomic layers. This work investigates the surfaces of clean Se-terminated Bi_2Se_3 and after a Bi bilayer has been grown on top by molecular beam epitaxy (MBE). Molecular dynamics (MD) simulations of ICISS are compared to the experimental data in order to ascertain the surface structures.

12:00pm **SS+2D-WeM13 Feature Scale Simulation for Materials Processing***,* ***Paul Moroz****,* TEL Technology Center, America, LLC*; D.J. Moroz,* University of Pennsylvania

Modern materials processing often includes complex chemistries and surface interactions, and variety of species incoming to the wafer from gas and/or plasma in the chamber. It also often involves many time-steps, each one utilizing different chemistry and different gas/plasma parameters resulting in time-varying composition of fluxes coming to the wafer, and different energy and angular distributions of incoming species. Chemically or physically active species interact with material surfaces, generally resulting in etching, deposition, and implantation, and such processes might even happen together at the same time. The FPS3D feature scale simulator [1-3] is capable of handling very different and complex cases due to its special structure and numerical techniques, from atomic layer etching and atomic layer deposition to large-scale Bosch processing. Numerical models of surface and molecular interactions are flexible enough to describe most general cases. For this presentation, we selected three types of simulation cases. The first type considers simulation of mostly etching and implantation, such as during Si etching by chlorine-argon plasma. The 2nd type considers ALE (atomic layer etch) when etching is done by a cyclic process of surface passivation/activation with the following process of etching/removal of a single atomic layer per cycle or per a few cycles, allowing ultimate processing accuracy. The 3rd type of simulations considers deposition cases, such as Cu seed layer deposition. Some results will be presented for 2D simulations and some others – for 3D simulations.

References:

[1] P. Moroz, IEEE Trans. on Plasma Science, **39** (2011) 2804.

[2] P. Moroz, D. J. Moroz, ECS Transactions, **50** (2013) 61.

[3] P. Moroz, D. J. Moroz, J. Physics: CS **550** (2014) 012030.

Author Index

Bold page numbers indicate presenter