

Tuesday Afternoon, November 10, 2009

Surface Science

Room: M - Session SS2-TuA

Wide Band Gap Semiconductors

Moderator: V. Bermudez, Naval Research Laboratory

2:00pm **SS2-TuA1 The Functionalization of Semiconductor Surfaces with Hemin**, *M. Losurdo*, IMP-CNR, Italy, *S.D. Wolter*, Duke University, *M. Giangregorio*, IMP-CNR, Italy, *T.H. Kim*, Duke University, *G.V. Bianco*, *P. Capezzuto*, *G. Bruno*, IMP-CNR, Italy, *A.S. Brown*, Duke University

Selective and sensitive detection of Nitric Oxide (NO) with a device that will monitor its concentration continuously for biological, environmental, and defense applications is highly desirable. One method of accomplishing this detection, is to functionalize a semiconductor surface with metaloporphyrin groups. Specific metaloporphyrins may be chosen for analyte selectivity. Heme, Fe-Protoporphyrin IX (hemin), for example, binds NO with much greater affinity, than to other gases such as O₂ and CO.

Herein, we present and discuss the semiconductor surface and interface chemistry involved in the chemisorption of hemin on III-V surfaces including InP, GaAs, GaN and on group-IV semiconductors including SiC and Si.

The peculiarity of our study is the use of spectroscopic ellipsometry for the monitoring of surface coverage and interface phenomena. Ellipsometry data are corroborated by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and electrical force microscopy. We discuss the dependence of semiconductor surface treatments e.g. native oxide, chemical treatments, passivating processes whose role is pre-conditioning the surface with -H or -NH terminal groups) on the self-assembling of the functionalizing biomolecules, and of the concentration of the hemin solution and chemistry duration on the chemistry and kinetics of the various semiconductor functionalization. We report also on the effect of benzoic acid addition to the hemin solution as a spacer to prevent formation of hemin aggregates in favor of normal-to-surface hemin orientation. By investigating a number of semiconductor base systems with a gap ranging in a broad range from 0.4 eV (InAs) to 3.4 eV (GaN) we demonstrate for the first time the correlation existing between the sensing activity and the semiconductor gap. This correlation might be useful to choose the appropriate semiconductor-based platform for a target sensing application. A correlation between the band gap of the semiconductors, the surface binding sites and the efficacy of functionalization is established and discussed.

This work is supported by the 7FP European Project NanoCharM (Multifunctional NanoMaterial Characterization exploiting ellipsometry and polarimetry)

2:20pm **SS2-TuA2 Photoelectrochemical Etching of a Non-Polar GaN LED**, *H.-Y. Kim*, Korea University, South Korea, *M.A. Mastro*, *C.R. Eddy, Jr.*, US Naval Research Laboratory, *J. Kim*, Korea University, South Korea

Light emitting diode (LED) structures fabricated from GaN-based material grown from along the polar c-axis possess a large polarization field within the active quantum well that hampers the efficiency of the device. This internal electric field separates the electrons and holes, which reduces the recombination rate in the quantum well (QW). To improve the light emission efficiency, we fabricated QW-LEDs from GaN-based material grown in the non-polar a-plane on r-plane sapphire. Implementing this approach to enhance the internal quantum efficiency on commercially available 2-inch r-plane sapphire required the development of a medium temperature AlN/GaN buffer layer scheme. Not only improved internal efficiency but also improved external efficiency is required to achieve high brightness LEDs. To date, the only widely applied technique to enhance the extraction of light from commercial polar GaN LEDs is to roughen the surface by dry or wet etching. We developed a photoelectrochemical (PEC) etching approach for the a-plane non-polar GaN LED. The samples were dipped into the KOH solution and exposed to UV light generated from a mercury lamp. A detailed investigation was conducted into the effect KOH concentration as well as the intensity of UV exposure on the etch rate and morphology of the surface. The PEC etching of the asymmetric bond structure along the [0001] and [1-100] directions generated the elongated dimples and roof-shape pillars. The density of the pillars and the width of the dimples increased with increased etching time. The dimples and pillars (surface texturing) on the surface provides an ensemble of angles for light to escape that is normally trapped within the crystal. Photoluminescence

measurements were conducted to investigate the relationship between extraction efficiency and surface texturing by this PEC etching technique.

2:40pm **SS2-TuA3 Surface Photovoltage and Band Bending in GaN**, *A.A. Baski*, *M.A. Foussekis*, *M.A. Reshchikov*, Virginia Commonwealth University **INVITED**

Although GaN is a wide-band gap semiconductor being successfully utilized in high-temperature and optoelectronic devices, the influence of surface effects such as band bending on the electrical and optical properties of GaN is not yet well understood. It is known that negative surface charge on air-exposed, undoped n-type GaN causes a substantial upward band bending of 0.4 – 1.5 eV. This band bending can be reduced by 0.3 to 0.9 eV during UV illumination, known as surface photovoltage (SPV), due to the accumulation of photo-generated holes at the surface. We have investigated the dependence of the SPV on illumination intensity and wavelength, as well as its transients after turning on and off illumination, using a Kelvin probe mounted in an optical cryostat. As expected, the initial SPV rise is slow at low illumination intensities and fast at higher intensities, where its initial slope is a linear function of illumination intensity. The SPV signal in air ambient under UV illumination increases within seconds to a maximum (0.4 to 0.7 V), but then gradually decreases during illumination. A similar behavior occurs in an oxygen environment (but not nitrogen), indicating that surface oxygen species are the primary component responsible for the observed SPV decrease. In vacuum, the SPV signal quickly increases but then slowly increases under UV illumination. This SPV behavior is consistent with the photo-induced adsorption of negatively charged oxygen species in air and their desorption in vacuum. After ceasing illumination, the SPV decays nearly logarithmically regardless of environment, but requires substantially longer to reach its dark value after extended illumination in vacuum.

We explain the transient and steady-state SPV under UV illumination using both internal and external mechanisms. The internal mechanism involves photogenerated holes that accumulate at surface states and recombine with free electrons from the bulk, whereas the external mechanism involves electrons that tunnel through a thin oxide layer and are captured by surface species, resulting in chemisorption. Our proposed phenomenological model quantitatively explains SPV data for low intensity UV light using only the internal mechanism; however, illumination at high intensities requires the inclusion of photo-induced chemisorption or desorption processes. Our studies to date have focused on n-type GaN, but we have preliminary data for p-type GaN indicating an initial downward band bending of ~1 eV and an unexpected increase in band bending under UV illumination. Studies of the band bending and SPV transients in different ambients are in progress and will be reported as well.

4:00pm **SS2-TuA7 Adsorption Processes on Silicon Carbide Surfaces**, *J. Pollmann*, Universitaet Muenster, Germany **INVITED**

Many experimental and theoretical studies of adsorption processes on semiconductors have employed Si(001) as a prototype substrate surface. The ionic group IV compound semiconductor silicon carbide (SiC), which is of large fundamental interest and of high application potential for electronic devices and sensors, offers particularly interesting new degrees of freedom for adsorption because of its different lattice constant and its rich variety of surface reconstructions giving rise to very amazing adsorption behaviour. For example, molecular hydrogen adsorbs dissociatively on SiC(001)-c(4x2) while it does not adsorb on SiC(001)-(3x2) at room temperature although both surfaces are characterized by similar surface dimers. Likewise the covalent attachment of organic layers to the SiC(001)-(3x2) surface, contrary to the Si(001)-(2x1) surface, gives rise to structurally well-defined configurations that can play a key role in organic functionalization. Incorporating new functionalities at SiC surfaces by adsorption of hydrogen or hydrocarbons requires a detailed understanding of the adsorbate-surface structure and its properties. In this talk adsorption of hydrogen, acetylene, ethylene and benzene on SiC(001) surfaces will be discussed. Scrutinizing a number of conceivable reaction scenarios within first-principles theory allows us to follow surface reactions on a microscopic level giving access to reaction mechanisms, transition states, barrier heights and adsorption energies and thus to identify the physical origin and nature of the peculiar adsorption behavior of SiC(001) surfaces. The theoretical results will be reviewed and discussed in comparison with available experimental data, as well as results for related adsorption processes on the Si(001)-(2x1) surface.

5:00pm **SS2-TuA10 Temperature Stabilised Surface Reconstructions in Humid Atmospheres and pH-dependent Stabilization Mechanism at Polar ZnO(0001) -Zn Surfaces**, *M. Valtiner, M. Todorova, J. Neugebauer*, Max-Planck-Institute für Eisenforschung GmbH, Germany, *G. Grundmeier*, University of Paderborn, Germany

The surface chemistry of oxides in humid atmospheres and in water based electrolytes (as e.g. oxide dissolution promoting effects of H⁺ and OH⁻) is an important aspect of molecular adhesion and related phenomena. Preparation and characterization of atomically well-defined oxide/electrolyte model interfaces, which allow well-defined molecular adhesion studies, are the most challenging issue in this context. Therefore, this contribution will focus of experimental results of the preparation of single crystalline ZnO(0001)-Zn model surfaces in humid atmospheres and complementary DFT-based ab-initio thermodynamics studies.

The main focus is the preparation and characterisation of surfaces, which are well defined on an atomic scale. The atomic structure of the polar ZnO(0001) surfaces in dry and humid oxygen environment was studied by diffraction experiments and density-functional theory in combination with atomistic thermodynamics. Our results indicate that for similar stoichiometries a large number of very different, but energetically almost degenerate reconstructions exist. Thus vibrational entropy, which could be safely neglected for most semi-conductor surfaces, becomes dominant giving rise to a hitherto not reported strong dependence of surface phase diagrams on temperature. Based on this insight we are able to consistently describe and explain the experimentally observed surface structures on polar ZnO(0001) surfaces [1,2].

Moreover, it will be shown that ZnO(0001)-Zn surfaces are stable and single crystalline within a wide pH range. An in-situ AFM study of the acidic dissolution allowed a nanoscale imaging of the dissolution process and hence a mechanistic understanding of the dissolution process of ZnO can be supported on a nanoscopic level [3]. Finally, first results of combining single molecule adhesion measurements with these single crystalline substrates will be highlighted.

[1] M. Valtiner, S. Borodin, G. Grundmeier; *Physical Chemistry Chemical Physics*, 9(19), (2007) 2406-2412.

[2] M.Valtiner, M. Todorova, G.Grundmeier, and J. Neugebauer; submitted to *Physical Review Letters*.

[3] M. Valtiner, S. Borodin, G. Grundmeier; *Langmuir*, 24(10),(2008) 5350-5358.

5:20pm **SS2-TuA11 Electronic Structure of Zinc and Free-Base Tetraphenylporphyrin Derivatives Adsorbed on TiO₂(110) and ZnO(11-20) Surfaces for Application in Dye Sensitized Solar Cells**, *S. Katalinic, S. Rangan, R. Thorpe, R.A. Bartynski, J. Rochford, K. Chitre, E. Galoppini*, Rutgers University

Metalloporphyrins play an essential role in photosynthetic mechanisms and therefore are natural candidates for electron transfer mediator in dye sensitized solar cells (DSSCs). Among the possible metalloporphyrins, the zinc tetraphenylporphyrins (ZnTPP) derivatives have been found to have similar electron injection and charge recombination properties as the important standard ruthenium dye N3 for DSSCs, as well as reasonable performances using TiO₂ or ZnO as substrates.

Due to a strong decoupling of the meso-phenyls from the main porphyrin macrocycle, the optical absorption properties of the ZnTPP derivatives are found relatively insensitive to the meso-phenyls functionalization. As a consequence, the adsorption geometry on the surface, as well as the molecule-molecule interaction, can be altered independently of the absorption properties.

Using direct and inverse photoemission spectroscopy we have measured the occupied and unoccupied electronic states of several zinc (and free-base for comparison) tetraphenylporphyrin derivatives adsorbed on single crystals TiO₂ and ZnO surfaces. From this, the alignment of the molecular levels (in particular the frontier orbitals) with respect to the substrate band edges can be directly determined. For a full interpretation of the electronic structure of such molecular adsorbates, we have compared our measurements to ab-initio calculations of the density of states. In addition to spectroscopic surface averaged probes, we have used scanning tunneling microscopy to study the local bonding geometries at the surface of the semiconductors. Recent results will be presented and compared to those available in the literature.

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