

Thursday Morning, October 23, 2008

Biological, Organic, and Soft Materials Focus Topic

Room: 201 - Session BO+EM+BI+NC-ThM

Semiconducting Biointerfaces and Sensors

Moderator: L.J. Brillson, Ohio State University

8:00am **BO+EM+BI+NC-ThM1 AlGaIn/GaN HEMT And ZnO Nanorod Based Sensors for Chemical and Bio Applications**, *B.S. Kang, H.T. Wang, K.C. Chen, Y.L. Wang, T. Lele, J. Lin, S.J. Pearton, F. Ren*, University of Florida

AlGaIn/GaN high electron mobility transistor based sensors are good candidates for low cost, handheld, and wireless chemical and biomedical sensor due to their excellent thermal as well as chemical stability and sensitivity to the changes of ambient. The electrons in the AlGaIn/GaN HEMT two-dimensional electron gas (2DEG) channel are induced by piezoelectric and spontaneous polarization effects and there is no dopant needed. There are positive counter charges at the AlGaIn surface layer induced by the 2DEG. Any slight changes in the ambient of the AlGaIn/GaN HEMT affect the surface charges of the AlGaIn/GaN HEMT. These changes in the surface charge are transduced into a change in the concentration of the 2DEG in the AlGaIn/GaN HEMTs. We have demonstrated AlGaIn/GaN HEMT based individual sensors for protein, DNA, kidney injury molecules, prostate cancer, pH values of the solutions, pH in the exhaled breath condensate, and mercury ions with specific surface functionalizations. We have also demonstrated ZnO nanorod based sensors to detect UV, hydrogen, carbon monoxide and ammonium. Recently, we integrated ZnO nanorods with AlGaIn/GaN HEMT to detect glucose in the breath condensate. This approach makes a possibility of integrating AlGaIn/GaN HEMT based sensors with ZnO nanorod sensors on a single "smart sensor chip" with the techniques of selective area functionalization and microfluidic device approaches. This smart sensor chip can be mounted on a handheld, portable, wireless transmitter circuit board.

8:20am **BO+EM+BI+NC-ThM2 Label-Free Dual Sensing of DNA-Molecules using GaN Nanowires**, *A. Ganguly, C.-P. Chen*, National Taiwan University, *K.H. Chen*, Academia Sinica, Taiwan, *L.C. Chen*, National Taiwan University

GaN, a leading optoelectronic material, is also known to be non-toxic and bio-compatible. Interestingly, this material in the form of nanowires (NWs), with the advantages of large surface-to-volume ratio and direct electrical-path due to surface-induced spatial-separation of charge-carriers, could possess high sensitivity to the local environment, hence to the surface-immobilized biomolecules. Here, we report the GaN NWs possess high bio-binding efficiency and provide a platform for in situ, label-free, and rapid (assay-time within 2 hours) detection of DNA-molecules with dual-sensing capability (electrochemical and optical). Both electrochemical (EC) and optical (photoluminescence, PL) measurements showed clear distinction of pristine GaN NWs with probe-DNA (pLF) immobilization, and after further hybridization, employing a popular target-DNA with anthrax lethal factor sequence (LF). In label-free condition, both EC and PL-based techniques exhibited high sensitivity, without any little effort to optimize the sensing-condition, up to nM and pM of concentrations, respectively for the recognition of LF, with very low assay-time. Furthermore, successful application for detection of "hotspot"-mutations, related to human p53 tumor-suppressor gene, revealed excellent selectivity and specificity towards the fully-complementary targets, down to pM concentration, even in presence of mutations and non-complementary strands, suggesting the potential pragmatic application in complex clinical samples. The simplicity in detection-method, without any requirement of extra step/modification in both probe and target-systems, and simultaneously, the unique label-free dual-detection capability of GaN NWs, with excellent selectivity and sensitivity, can make them a promising choice of transducers, even in clinical application.

8:40am **BO+EM+BI+NC-ThM3 GaN Field Effect Transistors for Biosensor Applications**, *W. Lu*, The Ohio State University **INVITED**

Biosensors based on electrical field effect transistors (FETs) are of great research interests due to their properties of label free, low cost, small size, and easy integration to external circuitry electronics. Such biosensors have been fabricated on many semiconductor materials including Si, silicon on oxide, carbon nanotube, ZnO, etc. Si-based such biologically FETs (bioFETs) suffer from various difficulties such as limited sensitivity and current drift caused by degradation of gate dielectrics and chemical instability. Due to the chemical inertness and the high concentration of two dimensional electron gas (2DEG) at the AlGaIn/GaN interface, AlGaIn/GaN

heterojunction FETs have great potentials for detection of bioagents in biological buffers with high ionic strengths. In this paper, we will give an overview of recent research progress on GaN FET biosensors. The process and characterization of functionalization of AlGaIn surface for biosensing applications will be discussed. The detection of streptavidin (STA) and monokine induced by interferon γ (MIG) proteins and hybridization process of single strand DNAs by AlGaIn/GaN HFETs will be presented. Specifically, for STA detection, at different ionic strengths, the effect of Debye length on detection sensitivity has been demonstrated. No current change is observed for fully biotinylated STA, indicating that there is no non-specific binding. Furthermore, we have used open binding pockets of specifically-bound STA on the biotinylated surface as receptors for detection of biotinylated MIG proteins. The results show that the devices are capable of detecting of biotinylated MIGs at pathological concentrations even at physiological ion strengths. In part, this is due to the superior stability of the AlGaIn/GaN HFET platform in buffer, which results in sensor noise being sufficiently low to allow reproducible detection of protein analyte binding. For comparison, regular unbiotinylated MIG proteins gave no current change, indicating that there is no non-specific binding and the change of current is due to the charges transferred from charged analytes.

9:20am **BO+EM+BI+NC-ThM5 Surface Functionalization of ZnO Nanoparticles and Thin Films for Sensor Applications**, *L. Selegard, C. Vahlberg, F. Söderlind, V. Khranovskii, A. Lloyd Spetz, R. Yakimova, P.-O. Käll, K. Uvdal*, Linköping University, Sweden

A new procedure has been developed for functionalization of electrochemically produced ZnO nanoparticles. The core of the particles was characterized using TEM, PEEM and LEEM. Single crystal nanoparticles, with uniform spherical morphology with a size of approximately 50Å were obtained. The first aims of ZnO nanoparticle functionalization were to make a stabilizing molecular layer at the surface and to prepare for further linking possibilities, for use in different types of sensing applications. The functionalization process was investigated and the molecular layer was verified by XPS and FT-IR. Parallel studies on biofunctionalization of plane ZnO thin films were performed to obtain a suitable reference system. One of the molecules used for functionalization of the nanoparticle surface was (3-Mercaptopropyl)triethoxysilane (MPTS) as it enables further functionalization on the thiol part and as it has the possibility to form a stable network around the particles. The MPTS linking was investigated by XPS and NEXAFS. The XPS spectra of the functionalized particles showed significant signal from both Si and S verifying the presence of MPTS. XPS core level S2p spectrum further showed presence of SH groups, indicating that thiols was available for further linking processes. Another molecule of interest for nanoparticle functionalization is oleic acid. The strategy is then to coordinate the carboxyl groups to the surface and further linking will be based on hydrophobic interactions. The TEM and PEEM results, so far, indicated that the particles were not fully dispersed but the use of oleic acid showed a much smaller extent of agglomerated particles than for example MPTS. PEEM also showed that the oleic acid capped particles was much more heat stable than MPTS capped once. ZnO nanoparticles show two emission peaks, one band gap related UV-emission and one visible emission arising from oxygen vacancies. In this work fluorescence spectroscopy was used to study the emitted, visible light of the particles as a function of different surface modifications.

9:40am **BO+EM+BI+NC-ThM6 Surface Functionalization and Micropatterning of Ta₂O₅ Films Using Organo-silane and Atom Transfer Radical Polymerization(ATRP) Methods**, *W. Kulisch, D. Gilliland, G. Cecccone, L. Sirghi, F. Rossi, H. Rauscher*, European Commission Joint Research Center, Italy

Optical waveguide biosensors frequently require the use high refractive index thin films such as tantalum pentoxide to act as both as a light guide and as a surface on which active biomolecules can be covalently immobilized. In this work, a process for the room temperature deposition of Ta₂O₅ films onto silicon/silica and thermoplast substrates by reactive ion beam sputtering from a tantalum target has been developed. The resultant high refractive index films have been chemically and optically characterized and methods examined for the wet chemical modification of the oxide film to produce either reactive amino groups or low protein fouling polyethylene glycol (PEG) layers. In both cases the first step toward the functionalization of the as-grown films used either an oxygen plasma or to an UV/O₃ treatment to produce a clean and fully oxidized surface. Using these clean, active surfaces-NH₂ terminated SAMs could be routinely produced using a conventional silanization process using 3-aminopropyl trimethoxysilane (APTMS). To produce high density, low protein binding (anti-fouling)

layers a more sophisticated procedure based on surface initiated atom transfer radical polymerization (SI-ATRP) of poly(ethylenglycol)methacrylate (PEGMA) has been used. In this method the oxide surface is firstly modified using a combination of poly(glycidylmethacrylate) (PGMA) and α -bromoisobutyryl bromide (BIB) to produce a surface rich in tethered α -bromoisobutyryl groups. These BIB groups can then be used as initiation sites for the growth of dense PEG films using the copper complex catalysed ATRP of PEGMA macromonomers. To characterize the final surfaces and to assist in the optimization of process, time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), contact angle measurements and atomic force microscopy (AFM) have been applied to samples after each step of the different processes. The effectiveness of the two processes will be demonstrated and examples given of methods by which the two methods have been combined for the production of fouling/non-fouling micropatterned surfaces.

10:40am **BO+EM+BI+NC-ThM9 Designing the Interfaces between Biomolecules and Semiconductor Substrates: From the C60 Buckyball Model System to Shape-Restricted DNA Molecules**, X. Zhang, A.V. Teplyakov, University of Delaware

A well-characterized interface based upon covalent binding between biomolecules and semiconductor surface was designed using the functionalized self-assembled monolayers (SAM) on Si(111) surface and specific shaped-restricted DNA molecules. This type of interface can serve as a prototype for the future devices in biosensing and single molecule spectroscopy. The spectroscopic and microscopic benchmarks were initially tested using fullerene C60 as a model to understand the attachment chemistry of large molecules with amine-terminated SAM on Si(111) surface. X-ray photoelectron spectroscopy (XPS) and Infrared spectroscopic (IR) studies, supported by computational investigation, verified the covalent attachment of C60 to the amine-terminated SAM on Si(111) surface. The atomic force microscopy (AFM) revealed the topography of the C60-modified surface with molecular resolution. The biomolecule/semiconductor interface was tailored with the same amine-terminated SAM on Si(111) surface and thiol-DNA molecules, which is achieved via a sulfosuccinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate (SSMCC) crosslinker molecule. The shape-restricted thiol-DNA is anchored to the surface through the formation of covalent bonds as confirmed by XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The AFM is used to visualize the well-defined and selective covalent binding of thiol-DNA molecules on SAM-covered Si(111). In addition, AFM and contact angle measurement are employed to study the change of the surface topography and the change of the surface hydrophilicity following each step of the DNA attachment chemistry on silicon.

11:00am **BO+EM+BI+NC-ThM10 The Effect of a Spacer Thiol on the Orientation and Hybridization Properties of 40mer DNA SAMs on Gold**, L.J. Gamble, P.-C. Nguyen, T. Weidner, University of Washington, D.W. Grainger, University of Utah, D.G. Castner, University of Washington

Methods for surface-immobilizing single-strand nucleic acids while preserving their original hybridization specificity with minimal non-specific interactions remain an important goal for improving the performance of surface bound DNA microarray and biosensor applications. Before the full potential of DNA microarrays can be realized, fundamental issues must be better understood, including how the crowding, conformation and orientation of immobilized DNA impacts DNA target hybridization efficiency. For detection of small amounts of DNA in a target solution, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. In this study the effect of backfill of mercaptohexanol (MCH) on 40mer thiolated single stranded DNA (SH-ssDNA) sequence orientation and hybridization efficiency is studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, sum frequency generation (SFG) vibrational spectroscopy, and surface plasmon resonance (SPR). While XPS and NEXAFS are both ultra-high vacuum techniques, SPR is a real-time solution based technique and SFG spectroscopy can be acquired both at the solid-air interface as well as the solid-liquid interface. While the 40mer DNA is longer and expected to be more disordered, the NEXAFS N k-edge spectra showed increased polarization dependence of the peaks at 401eV and 399eV for the 40mer sequence increased with an MCH backfill time of 1 hour. SFG spectroscopy results showed that incorporation of the MCH into the DNA monolayer resulted in an increase of the nucleotide related peaks at 2961 cm^{-1} and 3045 cm^{-1} which maximized at 1 hour MCH backfill. This evidence of orientation changes in the surface bound 40mer DNA will be correlated with hybridization data from SPR.

11:20am **BO+EM+BI+NC-ThM11 Anchoring and LT-STM/STS Characterization of Single Organic Molecules at Semiconducting and Insulating Surfaces**, M. Szymonski, A. Tekiel, S. Godlewski, G. Goryl, J. Prauzner-Bechcicki, J. Budzioch, Jagiellonian University, Poland

In recent years self-assembling of organic molecules deposited onto different surfaces have attracted considerable attention because of important applications in organic electronic technologies and prospects for development of single molecule computing devices. In this presentation we will report on our recent studies of initial stages of growth and organization of several organic molecules on reconstructed (001) surface of InSb, (011) and (110) surfaces of TiO₂, and on ultrathin KBr layers grown epitaxially on InSb(001). Among different organic molecules the perylene derivative -3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), often regarded as a model system for planar-stacking molecules, copper phthalocyanine (CuPc), violet landers (VL), and chiral helicene[11] molecules were studied by means of scanning tunneling microscopy (STM) at room and liquid nitrogen temperatures, nc-AFM at room temperature and low energy electron diffraction (LEED). It is shown that during initial stages of growth on InSb molecules often form chains parallel to [110] crystallographic direction of the c(8x2) reconstructed substrate. They are frequently attached to the lower terrace step edge, or some defects on the surface, indicating surprisingly weak interaction between the molecules and the substrate and their high mobility along [110] diffusion channel. Geometrical orientation of the molecules with respect to the reconstruction rows of the substrate will be discussed. We will present the images acquired with submolecular resolution, as well as images demonstrating the pinning effect of the molecular chains by surface charge density waves, and incorporation of the molecules into overall electronic structure of the system.

11:40am **BO+EM+BI+NC-ThM12 Molecular Self-Assembly of Functionalized Fullerenes on a Closed Packed Metal Surface**, B. Diaconescu, University of New Hampshire, T. Yang, S. Berber, Michigan State University, M. Jazdzzyk, G. Miller, University of New Hampshire, D. Tomanek, Michigan State University, K. Pohl, University of New Hampshire

Self-assembled organic thin films have a great number of practical applications, ranging from sensors and biological interfaces in medical implants to organic electronics and photovoltaics. Generally speaking, self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule-substrate and intermolecular interactions. Therefore, to control such self-assembly processes in a useful way, it is mandatory to understand how this balance reflects onto the SAM's final structure. Here, we present a combined STM and DFT study of the self-assembly of C60 molecules functionalized with long alkane chains, F-C60, on the (111) surface of silver. We find that F-C60 molecules lay down on the Ag surface and form a complex zigzag like pattern with an oblique unit cell of 4 nm by 2.5 nm and two molecules per basis. The C60s are placed at a larger than van der Waals distance. The symmetry of the functionalized C60 self-assembled monolayer is dictated by the alkane-surface interaction while the size of the unit cell is a consequence of the in-plane intermolecular interactions. These results show that C60s can be assembled in a two-dimensional and non-compact molecular array and suggest a way to control their surface density via appropriate chemical functionalization.

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