Tuesday Morning, November 1, 2005

Applied Surface Science
Room 206 - Session AS+BI-TuM

Surface Characterization of Organic and Biological Systems

Moderator: R.T. Haasch, University of Illinois

8:20am **AS+BI-TuM1 Synthesis and Characterization of Mixed Polymer Brush Films**, ***D.J. Dyer***, *J. Feng,* Southern Illinois University*; R.T. Haasch,* University of Illinois-Urbana Champaign*; V.-N. Wong,* Southern Illinois University **INVITED**

Chameleons respond to their environment by changing color so that they take on the characteristics of their surroundings. Smart organic films may also respond to environmental perturbations and adapt to their environment. In particular, polymer brush films have shown remarkable switching properties, especially when the films are within the ultra-thin region from 1-100 nm. These so-called polymer brushes are composed of polymers that are tethered to an inorganic substrate and may stretch out away from that substrate. Polymer brushes that are composed of more than one component are referred to as mixed, or binary brushes. Typically, the two different polymers are randomly distributed on the surface and exhibit phase-separation and interfacial morphology that is distinct from that of spin-cast blends of the same composition. This occurs because the brush chains are confined to the substrate and are forced into contact with nearby incompatible chains, whereas in a blend the polymer chains can more easily rearrange during annealing. Here we discuss the synthesis and characterization of mixed polymer brushes on silicon and gold substrates. One of the major challenges we face is the quantification of the bulk film composition as compared to the air/liquid interface. For this we use a tandem XPS/RAIRS strategy. Our paper will place an emphasis on amphiphilic systems where one polymer is hydrophilic and the other is hydrophobic. These results demonstrate that a mixed brush of polystyrene (PS) and polyacrylamide (PAAM) may switch from hydrophobic to hydrophilic in one minute at room temperature. Such rapid switching is highly unusual for mixed brushes.

9:00am **AS+BI-TuM3 Characterization of a Chemically Passivated GaAs Based Sensor Device in Air and Electrolytes**, *S.M. Luber,* Walter Schottky Institut, TU Muenchen, Germany*; D. Gassull,* TU Muenchen, Germany*; D. Schuh,* Universitaet Regensburg, Germany*; M. Tanaka,* TU Muenchen, Germany*;* ***M. Tornow****, G. Abstreiter,* Walter Schottky Institut, TU Muenchen, Germany

Functionalized field effect devices are promising candidates to act as smart substrates for sensor applications. For a use in biological systems a functional layer has to provide stability against electrochemical decomposition, and allow effective coupling of the surface potential to the conductive channel. We present a resistor device passivated with a 4'-substituted 4-mercaptobiphenyl (MBP) self-assembled monolayer (SAM) for sensing applications. Base material is a GaAs-AlGaAs heterostructure containing a quasi 2D electron gas 60nm beneath the surface. In the first part of our study we investigated the influence of the MBP-SAM on the electronic surface properties of n-doped GaAs samples employing the Kelvin probe technique. We changed the dipole moment of the MBP molecules using various substituents (-H, -OH, -CH@sub 3@) and found a linear effect on the electron affinity. In the second part we tested the stability of the resistor device based on the GaAs-AlGaAs heterostructure in aqueous solutions. Whereas a bare device degraded rapidly the coated samples showed a remarkable increase in stability. Furthermore we characterized samples coated with monolayers with CH@sub 3@ (MBP-CH@sub 3@) and OH (MBP-OH) substituents in buffered electrolyte solutions with varying pH. For the MBP-OH coated sample, a change in pH induced a change in the resistance of the device. Interestingly, the sample grafted with an MBP-CH@sub 3@ SAM also showed a clear response on pH which can be attributed to the adsorption of OH@super -@ ions on CH@sub 3@ groups.

9:20am **AS+BI-TuM4 Ion Beam Alignment of Nematic Liquid Crystal on PPV-layer**, ***S. Pylypenko***, *K. Artyushkova, J.E. Fulghum,* The University of New Mexico*; O. Buluy, T. Prokopenko, Y. Reznikov,* Institute of Physics of National Academy of Sciences, Ukraine

The development of LCD technologies requires homogeneous alignment of liquid crystals (LCs). The traditional rubbing procedure, consisting of unidirectional brushing of the aligning substrates, is quite reliable but has some drawbacks, including the production of electrostatic charges and dust during the rubbing. Ion and plasma-beam alignment are among the more promising candidates to replace the rubbing procedure. Ion beam alignment is based on an angularly selective destruction and rearrangement of the surface material as a result of ion bombardment, creating orientational order on the initially isotropic surface. Here we report on effective alignment of LCs on an ion-bombarded PPV layer. Glass substrates covered with a thin layer of PPV were irradiated using 2KeV Ar@super +@ ions for varying times. The irradiated substrates were used to assemble planar cells, and the gap was filled with nematic LC 5CB. The measured value of the anchoring energy of ~ 3 10@super -3@ erg cm-2 appeared to be one to two orders of magnitude less than the typical value produced by plasma/ion-alignment. We found enhancement of the stability of the PPV layer in the irradiated area. The strong interaction of 5CB molecules with the PPV surface caused dissolution of the PPV by the LC, and the PPV-layer was not affected by LC in the irradiated region. Three-dimensional characterization of the polymer by X-ray Photoelectron spectroscopy (XPS), Angle Resolved XPS (ARXPS), and Confocal Microscopy (CM) utilizing multivariate analysis (MVA) techniques were carried out to study the mechanism of PPV alignment after ion-beam bombardment. Our results demonstrate that ion-beam treatment provides uniform alignment of liquid crystals characterized by a weak anchoring.

9:40am **AS+BI-TuM5 Plasma Beam Alignment for Liquid-Crystal Displays**, ***Y.-F. Chang***, *C.-H. Lin, C.-W. Chen,* Industrial Technology Research Institute, Taiwan

Surface alignment of liquid crystals is an important issue in practical applications of liquid crystal (LC) cells on TFT-LCD process. The most common technique of LC alignment is an unidirectional rubbing on special polymer films which deposited on an conductive substrate such as ITO (Indium-Tin Oxide). The rubbing process has many disadvantages even though it has been widely used in the actual production of LCD. Thus, rub-free methods for LC alignment are strongly required in the next generation LCD technology. A number of non-contact LC alignment methods have been proposed in attempting to replace the rubbing process. And the well-known technique is ion beam irradiation proposed by IBM group. Another non-mechanical alignment technique, named photoalignment method, in which the UV light irradiation caused surface anisotropy of the bounding plates was studied for many years. The method was relatively simple, but the corresponding drawbacks such as weak anchoring energy as well as poor photo and thermal stability, may limit the application of this technology. In this research, a plasma beam alignment technique, in which the aligning substrate was treated with a flux of plasma that was extracted and accelerated electrostatically, was applied on the PI and diamond-like carbon (DLC) film. It is also a non-contact alignment process. The plasma flux was generated with a DC plasma source known as the anode layer thruster (ALT). The discharge channel was used to produce the sheet-like fluxes. The test panels (100 mm X 50mm) were fabricated with various plasma-beam processing parameters, w/o further passivation processes to study the alignment qualities including the pretilt angle, anchoring energy, VHR and Rdc as a function of these processing parameters. In addition, the measuring methods of these alignment qualities were also investigated in this study.

10:00am **AS+BI-TuM6 Measuring the Thickness of Organic/Polymer/Bio Films on Glass Substrates using Spectroscopic Ellipsometry**, ***H.G. Tompkins***, *T. Tiwald, C. Bungay,* J. A. Woollam Co., Inc.*; A.E. Hooper,* Motorola, Inc.

In this work we discuss a method of determining film thickness for film/substrate combination where the index of refraction of the film and substrate in the transparent spectral regions are almost identical. Common examples of this situation are organic/polymer/biological films on glass substrates. IR ellipsometry is used and we use weight gain to provide some necessary additional information for determining the optical functions for the film material. The spectral regions of strong molecular vibrations are then used for determining film thickness.

10:20am **AS+BI-TuM7 Applications of Surface Analysis in the Medical Device Industry**, ***A.M. Belu,*** Medtronic, Inc.

The surface is an important zone as it is the interface between a material of interest and the environment with which it interacts. For biomaterials and drug delivery systems, knowledge of interface chemistry is important for understanding how a material will interact with the biological environment of the body. For other materials, particularly those that are employed in the manufacture of medical devices, evaluation of the surface is important to further understand issues with welding, adhesion, contamination, discoloration, etc. This talk will highlight the power of surface analysis methods and how they are employed in the medical device industry. The analytical methods include TOF-SIMS and ESCA which allow chemical characterization of the uppermost ~75Å of a material. Scanning probe

microscopy (SPM) and laser profilometry are used to gain topographical information and to measure roughness of surfaces. A field emission scanning electron microscope (FE-SEM) allows high resolution imaging of surfaces with resolution capabilities to 1 nanometer. A low vacuum SEM further allows characterization of non-conductive, wet, and organic samples. SEM also has the capabilities for elemental identification and semi-quantitative analysis using an x-ray detector (EDS). Examples will be presented to demonstrate a range of surface analysis applications, from fundamental studies of biomaterials, to solving industrial problems. The power as well as the problems of data acquisition and interpretation will be highlighted with regards to each technique. Further, a comparison of all techniques will be made to help elucidate which method or methods are best for specific problems. Examples will include imaging the distribution of drug in a polymer coating (such as on stents), identifying contamination on medical devices (such as detergent residue on leads), evaluation of particles and defects, and characterization of surface chemical modification.

10:40am **AS+BI-TuM8 Microelectronic Multielectrode Interface for Evaluation of Living Cells**, ***H.D. Wanzenboeck***, *P. Hagl, K. Dominizi, E. Bertagnolli,* Vienna University of Technology, Austria; *E. Bogner, M. Wirth, F. Gabor,* University Vienna, Austria

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY ONLY PRESENT ONE (1) PAPER AT THE CONFERENCE.*****Tests on living cells are crucial in biomedical research, biotechnology , pharmacological diagnostics and medicine, but applied methods are often labor-intensive. Microelectronic technology has available sensitive techniques for automatized, continuous measurement and data interpretation. These advantages are not made use of due to the complex nature of the interface between the biological and microelectronic world. This work describes the fabrication and fundamental application of a functionalized biomaterial interface. For an interface to biological substances the choice of suitable substrate materials is decisive. A biological layer of human ephitelial cells (Caco-2) was grown in-vitro on the interface. The biocompatibility of inorganic and organic materials typically used in microelectronics was exploited. Metals, dielectrics and semiconductors were evaluated qualitatively by optical imaging and by scanning electron microscopy at variable pressure. A quantitative evaluation was performed with biochemical tests on cell proliferation and differentiation. Fundamental aspects of bio-interface engineering are investigated by interface analysis methods. In a second step 3-dimensionally patterned surfaces were explored as interface to the biological world. By microstructuring a miniaturisation of typical structures in the range of 20 µm down to 1 µm - smaller than the diameter of a living Caco2 cell - was performed. A functional microelectrode array proved to be an excellent bio-interface to living cells. The growth and behaviour of a Caco-2 cell layer on this array of multiple microelectrodes was studied by optical and electrical measurements. The electrical measurement through a single Caco-2 cell was recorded as impedance spectrum. The results contribute to the further understanding of the interactions between living cells and microelectronic biosensors. This work provides fundamentals to unite microelectronic engineering with in-vitro biological studies.

11:00am **AS+BI-TuM9 Chemical Imaging of Biological Cells and Tissues using TOF-SIMS**, ***P. Sjovall,*** SP Swedish National Testing and Research Institute, Sweden **INVITED**

Although time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been used for chemical imaging of cells and tissues for almost 10 years, recent advances (notably the new primary cluster ion sources) have the potential to lead to a new breakthrough in this area. To realize this, however, additional research is required, addressing issues like (i) sample integrity, (ii) lateral resolution / detection efficiency, and (iii) sample complexity. We have used TOF-SIMS to record the spatial distribution of lipids in freeze-dried mouse brain sections and in surface-adhering polymorphonuclear leukocytes (PMNLs). The mouse brain sections (14 µm thick, cryosectioned, placed on a glass or Si substrate and freeze-dried inside the TOF-SIMS instrument or in a separate vacuum chamber) were analyzed using Au@sub n@@super +@ and Bi@sub n@@super +@ primary ions. It is demonstrated that TOF-SIMS analysis can provide detailed images showing the distribution of a number of lipids on the tissue surface at lateral resolutions down to < 1 µm.@footnote 1@ It is also shown that migration of lipids may be a problem under certain sample preparation and analysis conditions. The PMNLs were analyzed using a chemical imprinting technique, in which the outermost molecular layers of the cells are transferred to a substrate surface by pressing the substrate against the cell sample. The advantage of this method is that the substrate surface can be selected and/or functionalized in a manner that optimizes the subsequent imaging TOF-SIMS analysis. For the PMNLs, chemical imprints were made on Ag substrates in order to improve the detection yield and specificity of the lipids using Ga@super +@ primary ions (taking advantage of the Ag cationization). The resulting images show a complementary localization of cholesterol (plasma membrane) and phosphocholine (nuclear membrane).@footnote 2@ @FootnoteText@ @footnote 1@ Anal. Chem. 2004, 76, 4271@footnote 2@ Anal. Chem. 2003, 75, 3429.

11:40am **AS+BI-TuM11 Studying the Effect of Spacer Thiol Chemistry, Orientation and Surface Coverage on the Hybridization Properties of Mixed DNA SAMs on Gold**, ***C.-Y. Lee,*** University of Washington; *P. Gong,* Colorado State University; *H.E. Canavan, L.J. Gamble,* University of Washington; *D.W. Grainger,* Colorado State University; *D.G. Castner,* University of Washington

Although it is desirable to capture DNA targets without purification from complex milieu (e.g., serum, tissue lysate) for microarray applications, this goal is often hindered by non-specific attachment of DNA and proteins. Minimizing nonspecific adsorption to biosensors and microarrays requires a non-fouling background. Furthermore, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. To achieve each of these goals, we evaluated the effect that two spacer thiols [11-mercapto-1-undecanol (MCU) and 11-mercapto-undecyl tetra ethylene glycol (OEG)] have on surfaces prepared using singled-stranded DNA containing a thiol anchor group (SH-ssDNA). These mixed DNA self-assembled monolayers (SAMs) have been studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), @super 32@P-radiolabeling, and surface plasmon resonance (SPR). Although XPS and radiolabeling indicate that SH-ssDNA surface coverage steadily decreases with longer exposure to the backfill molecules, NEXAFS indicates that polarization dependence peaks at short MCU and OEG exposure times (< 1h), after which polarization dependence decreases due to the loss of DNA from the surface. A comparison of hybridization responses from these probe surfaces was made using SPR by exposing the surfaces to complementary DNA in various concentrations of serum. SPR results indicate that although surfaces with MCU and OEG thiol spacers showed resistance towards non-specific DNA binding in pure buffer, hybridization efficiency is hindered by non-specific serum protein adsorption even at minimal serum concentration of 1%. Finally, differences in the hybridization property and protein resistance of the SH-ssDNA/MCU and SH-ssDNA/OEG mixed monolayer surfaces will be discussed.

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