

# Thursday Afternoon, October 18, 2007

## Plasma Science and Technology

Room: 607 - Session PS2+BI-ThA

## Plasmas in Bioscience

Moderator: P. Favia, University of Bari, Italy

2:00pm **PS2+BI-ThA1 Time-of-Flight Secondary Ion Mass Spectrometry Analysis of Fibrinogen Adsorbed to Low-Fouling Tetraglyme Surfaces**, L. Mayorga, R. Michel, D.G. Caster, T.A. Horbett, University of Washington

Antibody binding and ToF-SIMS were used to probe the conformation of fibrinogen (Fg) adsorbed to low and high fouling surfaces, including tetraglyme and FEP. Fg on implants plays a key role in the foreign body response (FBR) by mediating the adhesion of monocytes via the Mac-1 integrin.<sup>1</sup> PEO-like tetraglyme coatings generated via radio frequency glow discharge plasma display ultra-low Fg adsorption ( $\Gamma_{Fg} < 10 \text{ ng/cm}^2$ ) from low concentration blood plasma solutions and low monocyte adhesion.<sup>2</sup> However, subcutaneously implanted tetraglyme still exhibits FBR encapsulation. With 3 mg/ml Fg in buffer (with tracer amounts of <sup>125</sup>I-Fg added),  $\Gamma_{Fg}$  increased to 60 ng/cm<sup>2</sup> on tetraglyme and 800 ng/cm<sup>2</sup> on FEP. Nonetheless, the actual amount of  $\Gamma_{Fg}$  on glyme surfaces under any of the conditions tested is not enough to fully account for the observed monocyte adhesion in vitro. The Fg on glymes was relatively low, but adhesion was relatively high, suggesting that Fg might be in a more potent state on the glymes. To understand the role of Fg conformation in mediating monocyte adhesion, we used a monoclonal antibody to measure the degree of monocyte binding site ( $\gamma$  377-395) exposure on adsorbed Fg. Epitope exposure per ng of adsorbed Fg was highest on low-fouling tetraglyme samples pre-adsorbed with low concentration Fg. In addition, ToF-SIMS was used as in previous studies<sup>3</sup> to characterize the conformation of Fg adsorbed to the tetraglymes. By pairing these two different approaches to study the conformation of adsorbed Fg, we will be able to relate surface analysis results with cell and protein binding data, which will allow us to better understand protein-cell interactions in the FBR.

<sup>1</sup>Hu W-J, Eaton JW, and Tang L. Molecular basis of biomaterial-mediated foreign body reactions. *Blood* 2001; 98(4): 1231-1237.

<sup>2</sup>Shen MC, Martinson L, et al. PEO-like plasma polymerized tetraglyme surface interactions with leukocytes and proteins: in vitro and in vivo studies. *J. Biomater. Sci. Polymer Edn.* 2002; 13(4): 367-390.

<sup>3</sup>Michel R, Pasche S, Textor M, and Caster DG. Influence of PEG Architecture on Protein Adsorption and Conformation. *Langmuir* 2005; 21: 12327-12332.

2:20pm **PS2+BI-ThA2 Interaction of Peptide Ions with Self-Assembled Monolayer Surfaces**, J. Laskin, O. Hadjar, P. Wang, Z. Yang, Pacific Northwest National Laboratory

Interaction of ions with surfaces is an area of active research in surface science relevant to a broad range of other scientific disciplines such as materials science, mass spectrometry, imaging and spectroscopy. Our research is focused on fundamental understanding of interaction of hyperthermal (1-100 eV) peptide, protein and polymer ions with organic surfaces under ultrahigh vacuum conditions. Two major processes are dominant for this range of collision energies: reactive and non-reactive scattering of ions and ion loss on the surface as a result of neutralization or soft-landing (SL) of projectile ions. Scattering and deposition of large ions following collisions with SAM surfaces was studied using a unique Fourier transform ion cyclotron resonance mass spectrometer developed in our laboratory. Ion activation by collisions with surfaces is rather poorly characterized from a fundamentals perspective. We explored the effect of the physical and chemical properties of SAM surfaces on the energy transfer in collisions. Our studies demonstrated that energy distribution functions are well-represented by Maxwell-Boltzmann distributions indicating fast thermalization of ions by collisions. A notable discovery was a sharp transition between slow unimolecular decay of large ions at low collision energies and near-instantaneous decomposition (shattering) in higher energy surface collisions. Shattering of ions on surfaces opens up a variety of fragmentation pathways for large complex ions that are not accessible to conventional ion activation techniques. We have conducted first systematic study of several factors that affect SL of peptide ions on SAM surfaces. Deposition of peptide ions of different composition and charge state on SAM surfaces was followed by in situ and ex situ SIMS analysis. Peptide ions are attractive model systems that provide important insights on the behavior of soft landed proteins. We were able to measure for the first time the binding energy between peptide ions and hydrophobic SAM surfaces. We also demonstrated very strong binding of peptide ions to

hydrophilic surfaces and covalent linking of peptides to reactive SAMs. Fundamental principles derived from such studies of interaction of protonated peptides with hydrophobic or hydrophilic surfaces are relevant to the understanding of the transport of biomolecules through membranes in living organisms and provides a clear pathway for highly-selective preparation of biological surfaces.

2:40pm **PS2+BI-ThA3 A New Approach to Nano-Fabrication of Functional Structures : Wet Nanotechnology and Bio Nano Process**, I. Yamashita, Matsuhita Electric Industrial Co. Ltd. Japan **INVITED**

We proposed a new method for the fabrication of functional nano-structures in an aqueous solution, which could be used in semiconductor processes or electron devices and can be called a wet nanotechnology (WNT). The WNT employs aqueous solutions as the environments for nano-blocks, which are thermally agitated, to self-organize into the functional nano-structures. The final structures could be designed in the initial nano-block structures and functional nanostructures can be produced economically. This is the same with the way how the lives are carrying out in the nature. So far, we invented several processes using the WNT and proteins, which collectively we named Bio Nano Process (BNP).<sup>1</sup> So far, the BNP produced several key components of the electron devices. Firstly, a floating nanodots gate memory (FNGM) was produced employing a cage-shaped protein, apoferritin (collaborative project with Dr. Fuyuki at NAIST). Nanoparticles (NP) were biomineralized in the apoferritin cavity, which produced homogenous NPs such as CdSe, ZnSe, CdS, Co<sub>3</sub>O<sub>4</sub>, InOx, Fe<sub>2</sub>O<sub>3</sub> and so on. A 2D ordered array of the apoferritins with NP was made on the Si wafer by self-assembly and heat-treated. The obtained 2D ordered array of NPs was applied for the FNGM.<sup>3</sup> Secondly, we used 7nm Fe<sub>2</sub>O<sub>3</sub> NPs, which were produced and placed on Si wafer by the BNP, as the nanometric etching mask to fabricate Si single crystal nanocolumn (a collaborative project with Dr. Samukawa at Tohoku Univ). The neutral beam etching successfully produced single crystal Si columns with 7nm diameter and high aspect ratio.<sup>4</sup> We further extended the BNP application and produced a large bio-template for single electron transistor (SET).<sup>5</sup> A ball and spike type protein supramolecules which has a central cage-shaped protein and protruding spikes was produced by the self-assembly of genetically made chimera proteins. These experimental results demonstrated that the BNP can fabricate the inorganic nanostructure using protein supramolecules. The WNT and BNP are opening up a biological path to nano-electron devices.

<sup>1</sup>I. Yamashita, *Thin Solid Films*, 393, 12-18 (2001)

<sup>2</sup>K. Iwahori et al., *Biological path of nanoparticles synthesis*, Dekker Encyclopedia of Nanoscience and Nanotechnology, Taylor and Francis, 1 - 8 (2006)

<sup>3</sup>A. Miura et al., *Jpn. J. Appl Phys*, 45(1), L1-L3 (2006)

<sup>4</sup>T. Kubota, et al., *Appl. Phys. Lett.*, 84(9), 1555-1557, 2004

<sup>5</sup>K. Sugimoto et al., *Angw. Chem. Int. Ed.*, 45(17), 2725-2728, 2006.

3:40pm **PS2+BI-ThA6 Improvement of the Adhesion of PECVD-deposited DLC Films on Metals**, J.-C. Schauer, J. Winter, Ruhr-Universität Bochum, Germany

The coating of a material with a wear and corrosion resistant coating is required in many realms. Concerning biomedical applications for example a coating of implants made of shape memory alloys such as NiTi is needed to protect the implant against wear and corrosion and the surrounding tissue against the release of metal ions. One candidate for such a coating is a thin film of diamond like carbon (DLC, hard configuration of a-C:H), since it is very hard, wear resistant, has a low friction coefficient, is chemically inert and biocompatible. But up to the present the coating of most metals with a DLC film has shown many difficulties. The bad adhesion between substrate and DLC is due to the poor chemical binding between most metals and carbon and/or due to high internal stresses occurring in DLC films. One promising technique to overcome the problem of poor adhesion of the coating to the substrate is the deposition of a very thin interface layer on the substrate before the coating is deposited on top. By a correct material choice such an interface can replace weak coating-to-substrate bonds with strong coating-to-interface layer bonds and interface layer-to-substrate bonds. Another effect of the interface layer can be the reduction of internal stresses in the interface region. By the use of at least two layers on top of each other the probability of pinholes or defects going from the surface to the substrate is decreased. This is especially important if toxic substrates are to be coated. Therefore, we use a thin amorphous hydrogenated silicon (a-Si:H) film as an intermediate layer between metal and DLC film to enable the coating of metals with DLC films. Due to the formation of strong silicide bonds the adhesion of DLC films on metal is increased significantly. The thin films under investigation are deposited in a capacitively coupled discharge with acetylene and silane as precursor gases for the DLC and a-Si:H films, respectively. The a-Si:H films have a thickness of only several 10 nm, whereas the DLC films can have a thickness of 100 nm or more. It will be shown that an intermediate layer of a-Si:H significantly increases the

adhesion of DLC on metals and how the film properties of a-Si:H and DLC influence the strength of adhesion. The influence of different parameters like applied power, substrate temperature, hydrogen content in the films, and others on the adhesion of the films also under durability tests will be presented.

**4:00pm PS2+BI-ThA7 Polymeric Surfaces Chemical Modification by Low-Pressure Plasma Processes for Application to DNA Array Technology, P. Rivolo, Politecnico di Torino, Italy, S. Lo Bartolo, LaTEMAR, Ctr of Excellence funded by MIUR; Biodiversity SpA, Italy, D. Perrone, Lab. Materiali e Microsistemi, Italy; Politecnico di Torino, Italy, S. Fiorilli, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy, I. Vallini, LaTEMAR, Ctr of Excellence funded by MIUR; Biodiversity SpA, Italy, C. Ricciardi, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy, M. Quaglio, Lab. Materiali e Microsistemi, Italy; Politecnico di Torino, Italy, G. Mantero, Biodiversity SpA, Italy, C.F. Pirri, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy**

The low cost of production, the easy handling and the large variety of polymeric materials favour them as attractive candidates to replace classic glass slides in micro-array biomolecular diagnostics. However, the lack of reactive functional groups, at polymeric surfaces, makes difficult their use as substrates for immobilization of molecules such as DNA fragments, in either cDNA or oligodeoxyribonucleotide (ODN) format, for a variety of applications to DNA micro-array technology including microscale sequencing, mRNA expression monitoring and single nucleotide polymorphism analysis. In this contribution, modification of surface chemical properties of cyclo olefin copolymer (COC), polystyrene (PS), polyethylene (PE) and polycarbonate (PC) is reported. The surface of polymeric substrates, properly molded by hot embossing, was modified introducing monotype functional groups<sup>1</sup> and using them for subsequent covalent grafting of linker molecules, active for amino-oligonucleotide probes immobilization.<sup>2</sup> A first step consisting of non-equilibrium low-pressure air and water RF plasma was used to activate the polymer surface, forming oxidized species such as -C-O-, -C=O, -C-OH, -CHO, -COOH. Successively, a liquid-phase reduction by a NaBH<sub>4</sub> solution was carried out to increase the yield of -OH groups in order to enhance the amount of covalently grafted 3-aminopropylsilane (3-APTES), a reaction carried out by vapour-phase process.<sup>3</sup> The last step was performed by a liquid phase reaction between glutaraldehyde and amino-groups of grafted 3-APTES. After this, polymer surface shows -CHO species suitable for the reaction with the amino-modified probes. Characterization of the functionalised polymeric surfaces was performed by contact angle measurements and reflection-absorption infrared spectroscopy (RAIRS)<sup>4</sup>. Modification efficiency of different polymers substrates was evaluated by well-modified Arrayed Primer Extension (APEX) protocol with colorimetric and fluorimetric detection methods.

<sup>1</sup> J. Friedrich, W. Unger, A. Lippitz, I. Koprinarov, A. Ghode, S. H. Geng and G. Kühn, *Composite Interfaces* 10(2-3) (2003) 139-171

<sup>2</sup> Nathalie Zammatteo et al. *Anal. Biochemistry* 280 (2000) 143-150

<sup>3</sup> W. R. Ashurst, C. Carraro, R. Maboudian, W. Frey *Sensors and Actuators A* 104 (2003) 213-221

<sup>4</sup> G.-Y. Jung et al., *Langmuir* 21 (2005) 1158-1161.

**4:20pm PS2+BI-ThA8 Patterning of Plasma Polymers for Bioarrays, G. Mishra, S.L. McArthur, University of Sheffield, UK**

Modern day technological advancements have allowed us to overcome critical challenges posed in proteomic research. As a direct result of developments in miniaturisation and automation, the current market has seen ever growing numbers and varieties of high density arraying slides being used for proteome research and application. Needless to say that these developments have been matched with state of art instrumentation and data analysis packages to achieve true automated multiplex analysis. Yet, issues like non-specific adsorption of biomolecules to solid substrate and control over the orientation during immobilization need addressing. Key to these issues could be the precise control over surface modification and patterning. Plasma polymerisation presents a versatile approach to surface modification of these devices. The range of monomers available for plasma polymerisation makes this manufacturing approach even more suitable for use in systems where multiple coatings with specific properties are required for a single device. The ability to spatially define reactive regions to reduce non-specific background adsorption is integral to this project. In this study we use a range of patterning techniques including photolithography and physical masks and compare the resultant pattern resolution and chemical functionality using XPS, ToF-SIMS and AFM. Plasma polymerisation when used in conjunction with photolithography has allowed us to simultaneously obtain high spatial and chemical resolution. Multivariate analysis of ToF-SIMS spectral and image data has allowed us to critically study and address issues associated with the chemical specificity and spatial resolution of the multilayer patterning approach. Our results suggest that

complex multilayer plasma coatings can be produced without compromising the chemical properties of the deposited polymer layers.

**4:40pm PS2+BI-ThA9 BSA Adsorption onto Oxygen Plasma PTFE Modified Surfaces, B. Broze, N. Vandecasteele, Université Libre de Bruxelles, Belgium, P. Viville, Materia Nova, Belgium, R. Lazzaroni, M. Hecq, Université Mons Hainaut - Materia Nova, Belgium, D.G. Castner, University of Washington, F. Reniers, Université Libre de Bruxelles, Belgium**

The adsorption of bovine serum albumine on surfaces is usually a first good test for potential biological applications. In this study, PTFE surfaces were exposed to a remote RF oxygen plasma. The plasma was characterized using optical emission spectrometry, whereas the PTFE surface was characterized using monochromatized XPS, dynamic contact angle and atomic force microscopy. The modified surfaces are then exposed to BSA. The presence of protein was then evidenced by the presence of the N1s peak in the XPS spectrum, by AFM images, and by the change in the contact angle. We show that at low plasma power (or DC-bias) and short treatment times, the contact angle decreases, leading to slightly more hydrophilic surfaces. Small amounts of oxygen (up to 5%) are detected on the surface. BSA adsorbs on these surfaces. An increase in the plasma power leads to an increase of the sample roughness and to an increase of the hydrophobicity. On superhydrophobic (angles above 160°) surfaces, BSA does not adsorb any more. No oxygen is present in the XPS spectrum. A correlation was established between the change of the contact angle, the amount of adsorbed protein and the roughness. It is shown that the decrease of the contact angle, and the hysteresis between the advancing and receding angles are good probes for protein adsorption.

**5:00pm PS2+BI-ThA10 Composition and Structure Study of the AP Plasma Deposited Hydrophobic Thin Film, C. Chen, W. Hsieh, C. Liu, W. Hsu, C. Lin, Industrial Technology Research Institute, Taiwan**

In this study hydrophobic thin films were prepared by plasma enhanced chemical vapor deposition at atmospheric pressure by means of two layer compositions on the surface of glass. The bottoms were using Ar and hexamethyldisilazane (HMDSN) as the carrier and monomer gases respectively to deposit silicon oxide and offer microstructure. The deposited glasses were further coating a hydrophobic layer using fluoroalkylsilane (FAS) as the chemical precursor. Meanwhile, to evaluate the effects of fluorine contained of the water repellency of substrate, CF<sub>4</sub> was introducing into the plasma zone during plasma depositions. The chemical structure of the thin film was characterized using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopies (FTIR) measurement. Morphologies and topography of the coatings were examined by scanning micro spectroscopy (SEM) and atomic force microscopy (AFM). FTIR measurement indicated that a SiO<sub>2</sub> layer can successful deposit on the glass and the porosity of the thin films was direct proportion with thin film thickness. The SEM results indicated that the thickness of the thin films increasing almost linearly with coating times and the thickness was about 143nm after three times of deposition. AFM results reveal nano-clusters were well distributed on the surface after two layers deposition but introducing CF<sub>4</sub> during deposition will slightly reduced the roughness because of decompose reaction between CF<sub>4</sub> plasma and the Si atom in the thin films. The deconvolution of the C1s core-level spectra and atomic ratio from XPS measurement indicate FAS can be react and deposited on the top layer. The contact angles of the double layers was 134.0 degree which are great than traditional fluoro-polymer such as polytetrafluoroethylene (PTFE). Otherwise, bypass introducing CF<sub>4</sub> during plasma polymerization the contact angle will increased to 143.3 degree indicate the AP plasma can be used to deposit super hydrophobic thin film on the glass surface.

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