

Biomaterial Interfaces

Room 318/319 - Session BI+PS-FrM

Plasma Methods for Bio-interfaces

Moderator: E.R. Fisher, Colorado State University

8:20am **BI+PS-FrM1 Precision Chemical Control of Plasma Deposition for Smart Biosurfaces, B.D. Ratner, University of Washington** INVITED

In recent years, methods have evolved to deposit thin organic films from plasma environments that exhibit good control of chemistry along with the uniformity and substrate adhesion expected from plasma deposition. Three examples will be presented illustrating chemical control with special application to biomaterials. (1) Poly(N-isopropyl acrylamide) (pNIPAM) exhibits a solubility transition at 32 Å°C in an aqueous environment. When grafted onto a solid substrate, the pNIPAM phase transition produces a "smart" surface with strongly varying physical properties switchable with small temperature changes. Cells adhere and grow on ppNIPAM at 37Å°C and detach from the surface at room temperature. The ppNIPAM surfaces are non-toxic and excellent for cell growth. A microheater array can spatially control cell attachment to a ppNIPAM-treated chip. This suggests possibilities for cellomic and proteomic devices. (2) Since plasma environments destroy complex biomolecules, a new instrument has been constructed that combines electrospray ionization with plasma treatment of surfaces to produce a fast, efficient, flexible means to treat the surfaces of biomaterials with active biomolecules. The system has been successful in depositing intact, chemically bound hyaluronic acid (HA) onto plasma-activated stainless steel surfaces. (3) Poly(L-lactic acid) (PLLA) has been widely applied in tissue engineering scaffolds or for delivery of bioactive molecules, as it breaks down in the body to lactic acid, a component of the normal metabolism. The pulsed plasma deposition techniques has been used to form thin PLLA coatings using cyclic lactide monomer. Such films degrade in a phosphate buffer solution.

9:00am **BI+PS-FrM3 Investigation of Organic Monomers in Plasma-induced Chemical Micropatterning, G.Sh. Malkov, M.L. Godek, D.W. Grainger, E.R. Fisher, Colorado State University**

Plasma-enhanced chemical vapor deposition (PE-CVD) of organic films is a valuable technique for the surface modifications of polymeric biomaterials. Recently, plasma-based methods have been developed for the fabrication of chemical micropatterns, which have a number of applications, including production of multianalyte biosensors, diagnostic tests, DNA microchips, and genomic arrays. The generation of micropatterns by means of the plasma deposition of organic compounds through a transmission electron microscope (TEM) grid mask has been reported. Here, we have created various high fidelity micron-scale patterns of different chemistries using inductively coupled pulsed RF plasma deposition through a TEM grid with the following monomers: acrylic acid, N-vinyl-2-pyrrolidinone, 2-hydroxyethyl methacrylate, N-vinylformamide, allylamine, and hexylamine on PS coated with plasma deposited, highly hydrophobic fluorocarbon materials. SEM images of the patterned surfaces will be demonstrated. Physico-chemical properties of deposited polymeric materials were characterized using angle-resolved XPS, FTIR, spectroscopic ellipsometry, and static contact angle measurements on unpatterned samples, which were plasma treated under identical plasma conditions. Directed cell attachment studies have also been performed. NIH 3T3 fibroblast cells were used to test the cell adhesion and viability on the various patterned surfaces. PS coated with FC is biologically inert: cells do not adhere on this surface. In contrast, cells proliferate well on surfaces functionalized with organic monomers. Other cell culture experiments and biomolecule patterning will be discussed. @FootnoteText@@@footnote 1@ N.A. Bullet, R.D.Short et al. Surface and Interface Analysis. 2001, 31, 1074-1076.

9:20am **BI+PS-FrM4 Combining Pulsed RF Plasma Polymer Coatings with Avidin-Biotin Chemistry for On-Probe Affinity Capture Mass Spectrometry, G.R. Kinsel, M. Li, R.B. Timmons, University of Texas at Arlington**

Matrix assisted laser desorption / ionization mass spectrometry (MALDI-MS) has become a powerful analytical tool for the characterization of proteins. As the effectiveness of the MALDI method has advanced, the need for high-speed isolation and purification of targeted proteins in complex mixtures (e.g. culture media, serum or urine) has increased. The approach described in this presentation focuses on the use of RF plasma polymer coated MALDI probes as platforms for introduction of

avidin/biotin chemical modifications. Pulsed RF plasma deposition of allyl amine or vinyl carboxylic acid directly on the MALDI probe surface is used to produce amine modified and carboxylic acid modified surfaces, respectively. Control of the functional group density is achieved through changes in the duty cycle of the pulsed RF plasma. Both amine and carboxylic acid functionalized plasma polymer modified probe surfaces have been investigated as platforms for attachment of avidin or biotin. Testing of the surfaces for peptide/protein isolation based on the targeted properties is performed using various laboratory prepared control mixtures and mixtures obtained from biological sources. In all cases selective capture of the targeted protein/peptide was evaluated through the acquisition MALDI mass spectra using a Bruker BiFLEX linear MALDI TOFMS or a laboratory-constructed linear MALDI TOFMS. Data has been obtained from both avidin and biotin surfaces demonstrating the efficacy of these modified MALDI probe surfaces for achieving on-probe bioselective isolation of target compounds.

9:40am **BI+PS-FrM5 Chemical Modifications of PVC Endotracheal Tubes by RF-Oxygen Glow Discharge Pre-functionalization and NaOH/AgNO@sub 3@ Wet Treatments to Reduce Bacterial Adhesion, D.J. Balazs, K. Triandafillu, Swiss Federal Inst. of Tech., Switzerland; P. Wood, Univ. Hospital of Geneva, Switzerland; Y. Chevolut, Goemar Laboratories, France; C. van Delden, Univ. Hospital of Geneva, Switzerland; H. Harms, C. Hollenstein, H.J. Mathieu, Swiss Federal Inst. of Tech., Switzerland**

The use of silver as an antibacterial agent can be traced back to ancient times, and is currently used in several medical applications. Bacterial colonization of intubation tubes is responsible for 90% of all nosocomial pneumonia cases, 40 % of which lead to death, despite aggressive antibiotic therapy. We have developed an approach based on the surface modification of medical grade poly(vinyl chloride) (PVC) to create an anti-colonization surface, rich in silver ions. The modification consists of an oxygen plasma treatment, followed by a two step wet treatment in sodium hydroxide (NaOH) and silver nitrate (AgNO@sub 3@) solutions. XPS analysis and contact angle measurements were used to investigate the chemical nature and surface wettability of the films following each step of the modification. Saponification with NaOH of esters, like those of PVC plasticizers was determined to be a simple, irreversible method of hydrolysis, producing sodium carboxylate and phthalate salts. Following a subsequent incubation in the AgNO@sub 3@ solution, XPS showed evidence of a replacement reaction that produced a surface rich in silver ions. The potential of wet treatments that incorporate silver as a germicidal agent was demonstrated in bacterial and biofilm studies, using various *P. aeruginosa* strains. The native and O@sub 2@ pre-functionalized PVC surfaces submitted to the wet treatments exhibited a 100% reduction in initial bacterial adhesion. The efficacy of the wet treatment to reduce colonization over a longer period was demonstrated as 7-logarithmic drop in biofilm population at 24h and an 8-logarithmic reduction at 72 h, as compared to native PVC substrates. @FootnoteText@@@footnote 1@ R.O. Darouiche, (1999) Clin. Infect. Dis. 29, 1371-1377. @footnote 2@ J.L. Vincent, D.J. Bihari, et al., (1995) JAMA 274: 639-644. .

10:00am **BI+PS-FrM6 PECVD Growth and Ion Beam Modification of Polymer Films with Patterned Surface Charge Properties, A. Valsesia, M. Manso, G. Ceccone, D. Gilliland, F. Rossi, Joint Research Centre, Ispra, Italy**

The performance of polymer films in biomedical devices such as DNA arrays and other biosensors depends greatly on the ability to control their surface properties. In fact, surface features determine the ability of the polymer to immobilize a target biomolecule or to give this molecule an orientation towards adsorption. Plasma enhanced chemical vapor deposition (PECVD) of Polymers is an attractive way to produce this kind of films due to the high rate of functional groups obtained at energies ensuring film stability. The density of functional groups can be modified by an Ion Beam Modification. If this last treatment is performed through a mask, the surface remains with regions expressing different responses to chemical groups and environmental free charges (i.e. ions in solution). In this work we have studied the properties of two polymers with contrasted surface charge behavior. Allylamine (AlA) and Acrylic Acid (AcA) films were studied in parallel by Fourier transformed infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) outlining the changes occurred during plasma polymerization and ion beam modification. These spectroscopic results were correlated with wetting and surface charge behavior by performing contact angle and Z-potential measurements. Their stability and ability for protein adsorption was evaluated by using a quartz crystal microbalance (QCM-D). The possible interference with topographic features has been tested by observing the films in an atomic force

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microscope, which was further used to monitor electric fields in buffer solutions. From these results we conclude that the combination of PECVD and ion beam modification is an effective way for the growth of polymer films with controlled properties for bio-sensing applications.

10:20am BI+PS-FrM7 Growth of Biodegradable Thin Films by Methods of Pulsed Laser Deposition, J.M. Fitz-Gerald, A.L. Mercado, L. Zhigilei, R. Johnson, C.L. Fraser, University of Virginia; J.D. Talton, Nanotherapeutics, Inc.

Poly(DL-lactide-co-glycolide) (PLGA) is a biodegradable polymer with application in many areas of biomedical field ranging from contact lenses to sustained drug release formulation. In this research thin films (25 nm - 5 microns) of PLGA were deposited onto Si and NaCl wafers, in addition, a specific class of particulate materials (inhaled steroids) ranging from 1-5 microns in size were coated for in-vitro testing. All coatings were processed by both conventional pulsed laser deposition (PLD) and matrix-assisted pulsed laser evaporation (MAPLE) techniques. Film morphology, chemical structure, and decomposition effects were characterized by scanning electron microscopy (SEM), Fourier transform infrared infrared spectroscopy (FTIR), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and in-vitro dissolution.

10:40am BI+PS-FrM8 Study of RGD Peptide and Fibronectin Adsorption on Polymer Surfaces Micropatterned by Cold Plasma and Ion Beams, C. Satriano, University of Catania, Italy; M. Manso, Joint Research Centre, Ispra, Italy; N. Giambianco, University of Catania, Italy; G. Ceccone, D. Gilliland, F. Rossi, Joint Research Centre, Ispra, Italy; G. Marletta, University of Catania, Italy

Thin films of polycaprolactone (PCL) and polyhydroxymethylsiloxane (PHMS) were patterned by Ar⁺ ions beams or cold microwave Ar plasmas through Ni masks. The dimensions of the patterns stripes and pitches were typically between 30 and 100 μm. In the case of Ar⁺ irradiation, the two ion energies of 50 keV and 0.5 keV were used, with fluences ranging from 1x10¹⁴ to 5x10¹⁵ ions/cm². For plasma irradiation, the samples were placed on a grounded or RF biased sample holder (-50V), for different times. The surface structure and composition changes were characterized by spatially resolved X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surface roughness on the micro- and nanometer scale was determined by Atomic Force Microscopy (AFM). The surface charge and dispersive/polar forces distribution were determined by Zeta Potential (ZP) and Surface Free Energy (SFE) measurements respectively. Finally the change of thickness and visco-elastic properties of the films was investigated by the Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) technique. The adsorption of RGD peptide sequences and fibronectin was investigated as a function of the different treatment parameters, including ion energy and dose. The in-situ kinetics of adsorption and modeling of the viscoelastic properties of the adsorbed layers were studied by using QCM-D technique, while the chemical structure and lateral distribution of the adlayers were characterized ex situ by Small Spot XPS, ToF-SIMS Imaging measurements and AFM. The results showed that selective patterning of the adsorbed peptide and fibronectin could be achieved mainly in connection with the polar to dispersive ratio of the surface free energy. In particular, the surface modification seems to affect also the morphology adlayers.

11:00am BI+PS-FrM9 Chemical Modification of a Three-dimensional Tissue Engineering Polymeric Scaffold by Low-temperature Radio-frequency Plasma Treatment, S. Kumar, University of South Australia, Australia; R.St.C. Smart, University of South Australia; D.J. Simpson, University of South Australia and Seoul National University, Korea

The technique of low-temperature radio-frequency plasma has been employed for the chemical modification of Osteofoam, a three-dimensional polymeric (PLGA) tissue engineering scaffold material. The chemical modification in question was aimed at coating Osteofoam with a thin layer of silica, both on its surface as well as in its bulk. For this, Osteofoam cubes of dimensions 12 mm x 12 mm x 12 mm were treated with the plasma generated using tetraethoxysilane (TEOS) as the main precursor. The chemical modification thus achieved was investigated and quantified using the X-ray photoelectron spectroscopy technique, revealing the presence of silica both on the surface as well as in the bulk of Osteofoam samples. The XPS data also suggest that the plasma process developed and employed by us is relatively more efficient at modifying the sample surface than its bulk.

11:20am BI+PS-FrM10 Deposition of Amine Containing Films from Hyperthermal Silazane and Allyl Amine Ions, A. Choukourou, H. Biederman, Charles University, Czech Republic; E. Fuoco, S. Tepavcovic, L. Hanley, University of Illinois at Chicago

Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces. We have previously shown that fluorocarbon and siloxane ions can be employed for the growth and modification of organic thin films on polymer, semiconductor, and metal surfaces. These films are often similar in chemical composition to plasma polymers, due at least in part the presence of large, hyperthermal positive ions in many plasmas. This work deposits beams of mass-selected 5 - 200 eV silazane and allyl amine ions onto aluminum and silicon substrates. Silazane and allyl amine ions are produced by electron impact ionization of 1,3-divinyltetramethyldisilazane and allyl amine, respectively. These ion-deposited films are analyzed by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy. Chemical functionalization prior to XPS analysis permits the unique identification of primary and secondary amine groups. Secondary amine containing films are shown to form at low silazane ion energies whereas the higher ion energies lead to formation of more inorganic, silico-carbo-nitride-like films. Primary amines are produced by allyl amine ions at various energies. Films grown by allyl amine ion deposition are compared with those produced by plasma polymerization of allyl amine. Effects of film aging in air are also discussed. L. Hanley and S.B. Sinnott, Surf. Sci. 500, 500 (2002). P.N. Brookes, S. Fraser, R.D. Short, L. Hanley, E. Fuoco, A. Roberts, and S. Hutton, J. Elec. Spect. Rel. Phenom. 121, 281 (2001). E.R. Fuoco and L. Hanley, J. Appl. Phys. 92, 37 (2002).

11:40am BI+PS-FrM11 Plasma Chemistry of Allylamine for the Deposition of Nitrogen-Containing Organic Films, D.C. Guerin, Naval Research Laboratory, National Research Council; V.A. Shamamian, R.T. Holm, Naval Research Laboratory

We studied the chemistry of an allylamine/argon plasma for the deposition of nitrogen-containing organic films. We used in situ mass spectrometry to determine the identity of the molecular ion flux to the deposition surface. Our investigation showed that under the span of powers interrogated (30-100 W) the identity of the ion flux did not substantially change. The total ion current to the deposition surface increased linearly with plasma power. However, the molecular ion mass distribution changed with the plasma pressure. In lower-pressure plasmas, the predominant ions were generated by electron-impact ionization reactions. At higher pressures ions generated by ion-molecule reactions dominate the flux to the surface. We used appearance potential mass spectrometry to confirm the creation of NH₃ as a by-product of the ion-molecule reactions. The resulting films were characterized optically. The deposition rates were highly dependent on the plasma power. However, the indices of refraction were similar for the conditions studied. Infrared spectroscopy of the films showed that different plasma conditions resulted in only small changes in film structure. We determined that the film deposition mechanism was not controlled by plasma-ion chemistry. This contrasted with earlier results involving a saturated monomer. However, the film structure was highly dependent on the film thickness. The N-H signal increased greatly in the thicker films. Fluorescamine tagging of the amine groups in the films showed that the primary amine concentration was not well correlated to the intensity of the N-H stretch in the infrared spectra.

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