

Wednesday Morning, October 22, 2008

Biological, Organic, and Soft Materials Focus Topic

Room: 201 - Session BO+AS+BI+NC-WeM

Organized and Structured Organic Interfaces

Moderator: J.S. Shumaker-Parry, University of Utah

8:00am **BO+AS+BI+NC-WeM1 New Approaches to Chemical Lithography on the Micro- and Nanometer Length Scales**, *N. Ballav, S. Schilp*, Universität Heidelberg, Germany, *T. Winkler, H. Thomas, A. Terfort*, Philipps-Universität Marburg, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

The development of novel approaches for the fabrication of nanostructures and, in particular, chemical and biological patterns is an important technological and scientific challenge. One of the perspective methods applies a modification of chemisorbed monomolecular films - self-assembled monolayers (SAMs), which are well-ordered 2D-assemblies of long-chain molecules attached to a suitable substrate. A flexible molecular architecture of the SAM constituents allows us to use a wide range of substrates, whereas the molecular size of these constituents makes SAMs an ideal platform for the fabrication of micro- and nanostructures. We present here two new approaches for the fabrication of chemical patterns with aliphatic SAMs as templates. Both approaches rely upon electron beam or X-ray lithography, but require much lower patterning dose as compared to already available methods as, e.g., Chemical Lithography with aromatic templates. The first technique is based on irradiation-promoted exchange reaction (IPER) between the primary SAM template and potential molecular substituent and can utilize a broad variety of commercially available molecules. The key idea of the second method is irradiation-induced activation of amino tail groups of the primary amino-terminated SAM template. Feasibility of both techniques is demonstrated by the fabrication of complex polymer micro- and nanobrushes in a broad height range and, in the case of the IPER approach, by the preparation of micron-scale gradients of protein adhesion.

8:20am **BO+AS+BI+NC-WeM2 Reversible Activation of a Polyelectrolyte Brush: Responsive Monolayers**, *R. Steitz*, Hahn-Meitner-Institut Berlin, Germany, *V. Papaefthimiou*, TU Berlin, Germany, *J.U. Günther, C.A. Helm*, University of Greifswald, Germany, *S. Förster*, University of Hamburg, Germany, *G.H. Findenegg*, TU Berlin, Germany

Polyelectrolytes anchored on surfaces are important in various applications and are also a challenging topic for fundamental studies. In this work, a monolayer of the PEE114-b-PSS83 [(poly(ethyl ethylene)114-b-poly(styrene sulfonic acid)83] diblock copolymer was transferred from the air/water interface to a deuterated polystyrene coated silicon (dPS/Si) surface, for evaluation as a tunable polyelectrolyte brush containing system. The grafting density of the polymer film was controlled by changing the lateral pressure during the depositions. X-ray Reflectivity and AFM measurements showed that a homogeneous layer of the block copolymer was formed, whose thickness (maximum 8 nm) increased with increasing grafting density. Neutron reflectivity studies against aqueous solutions revealed a hydrophobic PEE layer attached on the dPS/Si surface, and a carpet/brush polystyrene sulfonate (PSS) double layer in water. The effect of salt concentration on the brush nanostructure was investigated in aqueous solutions containing 0-1 M NaCl. It was found that the brush thickness decreases for salt concentrations above 0.1 M. In addition, reversible activation of the brush by changing the ionic strength of the subphase was demonstrated. These results confirm a potential use as a stimuli-responsive polymer for both fundamental studies and biological applications.

9:20am **BO+AS+BI+NC-WeM5 Phase Stability of 2D and 3D Structures of Oligopyridines on HOPG Studied by Thermal Desorption Spectroscopy and Scanning Tunneling Microscopy**, *M. Roos, H.E. Hoster, R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen bonded 2D networks on graphite (HOPG) at both the solid/liquid^{1,2} and the solid/gas^{3,4} interface. As found by STM at both interfaces, these adlayer structures depend on the positions of the N-atoms within the molecules, which can be varied via the synthesis process.^{1,2} Complementary to the STM studies, we have performed temperature programmed desorption experiments of two different types of BTP molecules on HOPG. This revealed quantitative insights into phase stabilities of 2D (monolayer) and 3D (multilayer) phases. As to be expected from their large mass (618 amu) and correspondingly large moment of inertia, the translational and rotational degrees of freedom are found to play an important, even dominant role for the stability of more or less densely packed phases. This becomes apparent

in strongly differing pre-exponential factors for desorption out of 2D and 3D phases. In agreement with STM observations at 300 K, the most stable phase (i.e., the one with the lowest chemical potential) for both molecules is not a close packed hydrogen bonded one, but a dilute 2D gas with facilitated translation and planar rotation. In this picture, ordered, hydrogen bonded structures observed at room temperature are only stabilized by the strong molecule-substrate interaction that allows enforcing higher coverages that go along with the more densely packed, ordered structures.

¹ C. Meier et al., J Phys Chem B 109 (2005) 21015

² C. Meier et al., Angew.Chem.Int.Ed. 47 (2008) 3821

³ H. E. Hoster et al., Langmuir 23 (2007) 11570

⁴ M. Roos et al., Phys. Chem. Chem. Phys. 9 (2007) 5672.

9:40am **BO+AS+BI+NC-WeM6 Dielectric Spectroscopy for Biological Applications**, *C. Prodan, C. Bot*, New Jersey Institute of Technology

Dielectric spectroscopy (DS) is a widely used technique to study the properties of cells, proteins and DNA in a fast, label free and noninvasive way. It measures the complex dielectric permittivities as a function of frequency for the given sample. Cellular membrane potential is one of the most important parameters of a living cell and represents the voltage difference between the inside and outside of a cell. Usual values of the membrane potential are in the range of 100 mV. Across a membrane of 2nm thick, this means electric fields of half million V/cm. Theoretical studies have shown that the membrane potential plays a dominant role on the dielectric permittivity of a cell suspension at low frequencies (0Hz-1kHz). Thus the membrane potential can be obtained from a simple measurement of the cell suspension dispersion curves. This talk presents the application of DS to measure and monitor the membrane potential from the low frequency dispersion curves of living cell suspensions of bacteria and mammalian cells. This technique is tested against the standard techniques for measuring the membrane potential such as patch clamping or voltage sensitive dyes.

10:40am **BO+AS+BI+NC-WeM9 True All-Organic Epitaxy in Fashionable Organic Hetero-Junctions**, *G. Bussetti, C. Goletti, P. Chiaradia*, Università degli Studi di Roma Tor Vergata, Italy, *M. Campione, L. Raimondo, A. Sassella, A. Borghesi*, Università Milano-Bicocca, Italy

INVITED

The improvement of charge transport performances and the control of related electronic properties (a crucial step in the development of organic electronic devices) are strictly connected to the quality of the organic-organic interface, that up to now has been limited by three main problems: 1) the molecular package in organic crystals is significantly influenced by the sample size. It is a difficult task to grow a large single crystal: the substrates commonly used are often assemblies of smaller crystals with different orientations; 2) the chemical and physical properties of the substrate surface play a key role during the build-up of the organic layer. When an organic crystal is growing, significant changes (due to desorption, molecular readjustment, roughness variation, layer erosion, etc.) occur in the freshly deposited surface. Unfortunately, in-situ and real time spectroscopies are not yet commonly applied to monitor this complex phenomenology; 3) an effective thermodynamic strategy during the arrangement of the organic hetero-junction -as in inorganic Molecular Beam Epitaxy- (e.g., control of substrate temperature and sample growth rate, choice of single or multi-bunch growth, etc.) is still lacking in the deposition process. As a matter of fact, only recently a true all-organic epitaxy has been achieved. In this talk, the successful work and the most representative results we obtained in the last five years will be presented, showing that concrete possible solutions to the above mentioned points have been found. In particular, we have succeeded in growing different single organic crystals, namely α -quaterthiophene (α -4T), α -sexythiophene (α -6T), tetracene, rubrene, etc., with different shape, size (up to several square mm's) and orientation. An accurate investigation of the morphological and optical properties of the bare substrate as well as of the freshly grown ultra-thin organic layers has been performed. Our results demonstrate that the organic layer exhibits a high sensitivity to very low amount of contaminants. Moreover, we will show that it is possible to tune the crystal growth from a Stransky-Krastanov to a Frank-van der Merwe mode during the layer deposition of different organic compounds [α -4T, α -6T, tetracene, rubrene, etc.] by Organic Molecular Beam Epitaxy. In conclusion, the growth of various organic heterojunctions with epitaxial quality is now a gain result.

11:20am **BO+AS+BI+NC-WeM11 Modification of Self-Assembled Monolayer Surfaces Using Hyperthermal Ion Beams, J. Laskin, P. Wang, O. Hadjar**, Pacific Northwest National Laboratory **INVITED**

Collisions of ions with surfaces play an important role in a variety of scientific disciplines including surface science, materials science, mass spectrometry, imaging and spectroscopy. This presentation will focus on phenomena that occur during collisions of complex polyatomic ions with surfaces at hyperthermal energies with specific emphasis on ion deposition, charge transfer, bond making and bond breaking processes. Because in this energy regime the initial kinetic energy of the ion is commonly sufficient for breaking chemical bonds on the surface but is too low for significant penetration of a polyatomic ion into the surface, hyperthermal collisions are well suited for chemical modification of the outer layer of the surface without substantial perturbation of the bulk substrate. In addition, careful control of the properties of the ion beam can be used for very specific surface modification. Covalent and non-covalent immobilization of peptides using soft-landing of mass-selected ions onto inert and reactive self-assembled monolayer surfaces will be discussed. Fundamental principles derived from such studies 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.

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