

Wednesday Afternoon, November 6, 2002

Nanometer Structures

Room: C-207 - Session NS+EL-WeA

Nanolithography & Self Assembly

Moderator: P.S. Weiss, The Pennsylvania State University

2:00pm **NS+EL-WeA1 Recent Development in Nanoimprinting Lithography**, **L.J. Guo**, University of Michigan **INVITED**

Nanoimprinting lithography is an emerging technology that promises ultra-high resolution, high throughput and low cost. Unlike soft contact printing that uses an elastomer stamp, nanoimprinting uses a hard mold to create nanoscale features by directly imprinting into the polymer film at a temperature higher than its glass transition temperature (T_g). Sub-10 nm resolution and large area patterning have already been demonstrated in the past. This talk will present some recent development in nanoimprinting lithography, including imprinting at reduced temperature by using low T_g polymer materials; a reversed imprinting technique that enables "inking" of polymer materials onto a substrate, and patterning on non-flat surfaces without planarization, as well as the creation of simple 3D structures. This reversal nanoimprinting method also offers a unique advantage by allowing imprinting onto a flexible substrate that is otherwise difficult to spin-coat with polymer film, and we have demonstrated this by imprinting on a 50 mm thick flexible polyimide film. Nanoimprinting not only has the ability to pattern nanoscale features, but also it is compatible with polymer material processing. Based on these characteristics, we have applied it to two new applications. The first one is polymer micro-ring resonator photonic device fabricated by nanoimprinting, which is in the form of a micro-ring closely coupled to a waveguide, and offers unique properties such as narrow bandwidth filtering, high quality factor, compactness, and could find important applications in integrated photonic circuits. The second application is in organic polymer light emitting diodes (OP-LEDs), where we have developed a simple method based on nanoimprinting to define the OP-LEDs with pixel size ranging from nano- to micron-scale. The demonstration of those small size OP-LEDs indicates the possibility of fabricating ultra-high resolution OP-LEDs for applications such as micro-displays.

3:00pm **NS+EL-WeA4 Fabrication of Molecular Nanostructures by Scanning Near-Field Optical Lithography**, **K.S.L. Chong**, **S. Sun**, **G.J. Leggett**, University of Sheffield, UK

Nanoscale patterns of self-assembled monolayers (SAMs) on gold and silver can be fabricated by a new technique called scanning near-field photolithography (SNP).¹ In SNP, a 244 nm laser coupled to a scanning near-field optical microscope is used to carry out nanometre scale photopatterning of SAMs. The photooxidised SAMs can be dipped into a solution of a different thiol, which displaces the oxidised material and adsorbs at the surface. Chemical patterns with linewidths of 40 nm were routinely obtained though patterns as small as 25 nm have been observed by friction force microscopy. The oxidised pattern can also be transferred to the underlying substrate by wet etching where linewidths of 80 nm have been obtained on gold substrates. Because of the ease by which SAMs can be patterned by this method, SNP can be routinely used to create nanoscale molecular patterns. Nanoscale patterns in SAMs can be used as templates for the attachment of biomolecules offering another approach to the miniaturisation of biological devices. Preliminary data have shown that proteins may be successfully immobilised to micron-scale patterned monolayers created using similar photochemistry. These methods are currently being combined with SNP in order to create biological nanostructures.

¹Shuqing Sun, Karen S.L. Chong and Graham J. Leggett, *J. Am. Chem. Soc.*, 2002, 124, 2414.

3:20pm **NS+EL-WeA5 Photoinduced Anisotropy of Second-Harmonic Generation from Azobenzene-Modified Alkylsiloxane Monolayers**, **Y.W. Yi**, **T.E. Furtak**, Colorado School of Mines, **M.J. Farrow**, **D.M. Walba**, University of Colorado

Non-contact alignment of substrates in liquid crystal displays offers the advantage of reduced contamination and minimal surface charging. This approach also provides a means of reversible alignment after a device has been assembled. With this objective we have synthesized self-assembled monolayers based on dimethylaminoazobenzene units covalently attached to a glass surface by means of a short alkylsiloxane anchor (azo-SAM). The resulting architecture favors an orientation in which the axis of the azobenzene group should be nearly parallel to the surface with an isotropic azimuthal distribution. Under illumination with polarized UV light the trans-cis isomerization and subsequent relaxation serves to wiggle the

molecule into an orientation perpendicular to the UV optical field. We have tested this scenario using optical second harmonic generation. We are able to identify a surface order parameter that characterizes the photoalignment of the azobenzene group. These data correlate with the recently reported behavior of nematic liquid crystal cells containing one substrate treated with the same azo-SAM.¹ This work is supported by NSF MRSEC grant DMR-9809555.

¹"Liquid Crystal Alignment by Photo-Buffing Azo-SAMs", G. Fang, N. A. Clark, J. E. McClennan, M. Farrow, D. Walba, March Meeting of the American Physical Society, Indianapolis (3/20/20002).

3:40pm **NS+EL-WeA6 Nanostructuring of Hydrogenated Silicon Surfaces by Electron Beam Irradiation of Self-assembled Hydroxybiphenyl Monolayers**, **A. Küller**, **W. Geyer**, **V. Stadler**, Universität Heidelberg, Germany, **T. Weimann**, Physikalisch Technische Bundesanstalt, Germany, **W. Eck**, **A. Götzhäuser**, Universität Heidelberg, Germany

A new species of aromatic self assembled monolayers, hydroxy biphenyl, are formed on hydrogen terminated silicon and used as a negative tone electron beam resist. The formation of the monolayer and the electron induced modifications are observed by X-ray photoelectron spectroscopy. Nanometer patterns in the molecular layer were defined by low energy electron proximity printing as well as via conventional e-beam lithography. The patterns are transferred into silicon by a wet chemical etching process in KOH. The fabrication of patterns with lateral dimensions below 20 nm is demonstrated.

4:00pm **NS+EL-WeA7 Electrode Modification by Electron-induced Patterning of Self-assembled Monolayers**, **B. Völkel**, **G. Kaltenpoth**, **T. Felgenhauer**, **W. Geyer**, **H.T. Rong**, Universität Heidelberg, Germany, **M. Buck**, University of St Andrews, UK, **A. Götzhäuser**, Universität Heidelberg, Germany

Nanopatterns on electrode surfaces control the electrochemical deposition. An example is the formation of nanoscale dots or wires via the preferred nucleation at defects and step edges.¹ We present a method to artificially fabricate such electrochemical templates via coating of electrodes with self-assembled monolayers (SAMs) and subsequent patterning by electron beams. SAMs provide a flexible route to modify electrode surface properties via their molecular structure, ranging from inert alkane chains, which exhibit a blocking behavior, to redox active moieties. The e-beam patterning offers perspectives to generate arrays of microelectrodes with specific functionality. We coated gold electrodes with SAMs of ω -(4'-methyl-biphenyl-4-yl)-dodecylthiol (BP12) and hexadecanethiol (HDT) and patterned them by electron beam lithography. The subsequent copper deposition in an electrochemical cell revealed that the e-beam patterned alkanethiol behaves opposite than e-beam patterned biphenyl. Similar to the behavior of these materials as resists,² HDT acts as a "positive template" leading to copper deposition only on the irradiated parts. BP12 acts as a "negative template", where the irradiated biphenyl layer is cross linked and exhibits a blocking behavior,³ hence copper is only deposited on the non-irradiated parts. By using these effects well defined Cu nanostructures could be generated.

¹ M. P. Zach, K.H. Ng, R.G. Penner, *Science* 290, 2120 (2000).

² A. Götzhäuser, W. Geyer, V. Stadler, W. Eck, M. Grunze, K. Edinger, T. Weimann, P. Hinze, *J. Vac. Sci. Technol. B* 18, 3414 (2000).

³ T. Felgenhauer, C. Yan, H.T. Rong, A. Götzhäuser, M. Buck, *Appl. Phys. Lett.* 79, 3323 (2001).

4:20pm **NS+EL-WeA8 Electrochemically Controlled Film Formation of Self-assembled Monolayers of Biphenyl-based Thiols**, **I. Thom**, **B.J. Livesay**, St Andrews University, UK, **P. Cyganik**, Jagiellonian University, Poland, **M. Buck**, St Andrews University, UK

Usually self-assembled monolayers (SAMs) of thiols are prepared by mere immersion of the substrate in a solution containing the respective thiol. Whereas a number of preparation parameters such as the thiol concentration, temperature, immersion time, or solvent type have been investigated in some detail, no systematic studies have been performed on how the substrate potential affects the kinetics of film formation and the resulting SAM structure. Since the potential controls the bonding of a thiol to the substrate, i.e. its stability, the rate of adsorption/desorption and the mobility of the thiols are affected and, consequently, a pronounced influence of the potential can be expected. Using thiols which are characterized by a biphenyl unit and an alkane spacer chain between the aromatic moiety and the SH group we have studied the kinetics of film formation using nonlinear optical spectroscopies and scanning tunneling microscopy. Both the kinetics of film formation and the final film structure undergo significant changes ranging the potential from values near the reductive desorption of thiols to values around zero volts.

4:40pm **NS+EL-WeA9 Modification of Self-assembled Monolayers by Free Radical-dominant Plasma: The Effect of the Chain Length and the Substrate**, *M. Zharnikov, S. Frey, M. Grunze*, Universität Heidelberg, Germany, *M.-C. Wang, J.-D. Liao, C.-C. Weng*, Chung Yuan Christian University, Taiwan (ROC), *R. Klauser*, Synchrotron Radiation Research Center, Taiwan (ROC)

Synchrotron-based high-resolution photoelectron spectroscopy was applied to study the modification of aliphatic and aromatic thiol-derived self-assembled monolayers (SAMs) on (111) gold and silver substrates by a nitrogen-oxygen downstream microwave plasma. It was found that the plasma treatment does not result in a "soft" modification of SAMs, but in their massive damage and disordering. Contrary to the electron beam treatment, both the aliphatic and aromatic films became modified and damaged in a similar way, with the extent of the changes depending on the length of the molecular chains and, above all, on the substrate. For SAMs on Au a profound desorption of the entire SAM constituents and a complete fragmentation of the residual hydrocarbons is observed. For the SAMs on Ag only partial desorption and oxidation took place and, for short treatment times, the films remained practically intact. The desorption of molecular species was preceded by the oxidation of the pristine thiolates to weakly-bonded sulfones, which occurred after the penetration of chemically active oxygen species into the S/substrate interface via defect sites. Such a mechanism clearly explains the observed dependence of damage extent on the SAM thickness and emphasizes the importance of the strength of the thiolate-substrate bond. Thus, a stronger thiolate-substrate bond can be suggested for Ag as compared to the Au substrate. In addition, considering the similarity of the plasma-induced processes and UV-photooxidation, one can extend the major conclusions obtained for the plasma treatment to UV-photooxidation.

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