### Thursday Afternoon, October 23, 2008

#### Nanometer-scale Science and Technology Room: 311 - Session NS+NC-ThA

#### Nanolithography and Manipulation

Moderator: J.N. Randall, Zyvex Labs

2:00pm NS+NC-ThA1 Pattern Error Correction and Density Multiplication by Lithographically Guided Self Assembly, R. Ruiz, E.A. Dobisz, D.S. Kercher, T.R. Albrecht, Hitachi Global Storage Technologies Inc., H. Kang, F.A. Detcheverry, J.J. de Pablo, P.F. Nealey, University of Wisconsin INVITED

Patterned media for storage applications at densities beyond 1Tb/in<sup>2</sup> requires fabrication of periodic patterns at 27nm full pitch and smaller. Templating patterns at these dimensions is particularly challenging when considering the stringent quality restrictions imposed by storage applications in terms of feature size distribution, line edge roughness, placement and long-range ordering. We present here a guided self-assembly approach that combines e-beam lithography with block copolymer selfassembly. E-beam lithography is used to pre-pattern a guiding substrate defining features with registration and long-range orientational and translational order. A block copolymer film is applied on top of the guiding pattern. The uniformity of the self-assembled features effectively corrects noise and non-uniformities introduced by the e-beam and the e-beam resist. We use image processing to quantify the pattern quality rectification achieved by the block copolymer. We also use this guided self-assembly approach as a pattern density multiplier. The self-assembled pattern can be used to multiply the density of e-beam features by at least a factor of four. This density multiplication approach enables the possibility to pattern features at resolutions not accessible by state-of-the-art e-beam lithography but still taking full advantage of its registration and long-range ordering properties.

#### 2:40pm NS+NC-ThA3 Patterning Self-Assembled Monolayers of Thiols Down to the sub-10 nm Scale by Scanning Tunneling Microscopy, C. Shen, M. Buck, University of St. Andrews, UK

While self-assembled monolayers (SAMs) have opened up unprecedented opportunities for surface functionalisation and patterning, the generation of structured SAMs on the ultrasmall length scale remains a challenge. In this range scanning probe microscopies such as scanning near field optical microscopies (SNOM), STM and AFM play a crucial role as patterning tools. Depending on the techniques, different schemes of modification are applied, e.g., load and field induced modification for AFM and STM, respectively. Here we report our studies on STM based patterning using SAMs of (methyl-biphenyl-4-yl)-alkane thiols (BPn SAMs) on Au(111). Since these systems form layers of excellent structural quality they are promising systems for nanolithography. Patterns were generated by displacement of BPn molecules by alkane thiols. In contrast to the common approach, STM patterning was performed at voltages well below those of field induced disruption of the SAM. Since these rather gentle conditions of SAM modification do not result in major changes of the STM tip, the resulting SAM patterns could be analysed at molecular resolution. Lines as thin as 2.5 nm and dots below 20 nm2 can be straightforwardly produced. It is found that the structure of BPn SAM is reflected in its displacement behaviour. For example, (methyl-biphenyl-4-yl)-ethane thiol (BP2) which exhibits a rectangular unit cell exhibits a patterning anisotropy with a preferential displacement and differences between alternating rows of molecules along the <11-2> directions.

#### 3:00pm NS+NC-ThA4 A Novel Nanolithography Technique for Formation of Uniform Nanostructures, W. Wu, D. Dey, O. Memis, A. Katsnelson, H. Mohseni, Northwestern University

A novel nanolithography technique—Nanosphere Photolithography (NSP)—was demonstrated to generate a large area of highly uniform nanoholes or nanoposts of photoresist by utilizing the monolayer of hexagonally close packed silica microspheres as super-lenses on top of photoresist. Both our simulation and experimental results show that the size of the nanostructures generated is almost independent of the sphere sizes and hence extremely uniform patterns can be obtained. We also show that large areas of highly uniform nanoholes (~250 nm) and nanoposts (~300 nm) in multi metal stacks with the period of 1 um using the broadband wavelength of light centered about 400 nm. The nanoholes diameter in metal layers could be tuned by changing the under-cut strength. Using this method, the nanoholes with bottom diameters as small as 50 nm could be produced. The period and size of the nanostructures could be tuned independently by changing proper parameters. We were also able to

generate nanostructures within desired patterns by combining the NSP technique with standard photolithography masks during exposure. Our simulation results show that the sizes of the nanostructures can be further reduced using shorter wavelengths. This technique establishes a new paradigm for high throughput nano-lithography, allowing rapid, economical and simple creation of large areas of uniform nanostructures.

#### 3:20pm NS+NC-ThA5 Fabrication of Large Area Glass Submicron Pattern by Multibeam Interference Lithography and Reactive Ion Etching, H.S. Jee, University at Buffalo, A.P. Zhang, Zhejiang University, China, R. Burzynski, Laser Photonics Technology Inc., K.T. Kim, P.N. Prasad, Y.K. Yoon, University at Buffalo

Large area glass submicron patterns are important because of its advantages and great potentials for the applications of nanoimprint molding, diffraction mask patterning, gratings, diffractive waveguide devices, microfluidic channels, and lab on a chip. In this work, we use multibeam interference lithography using photoresist to fabricate two dimensional (2-D) submicron patterns covering a large glass substrate area and nano pattern transfer to the glass substrate using subsequent reactive ion etching (RIE). Three plane wave laser (532nm) beams are utilized for interference pattern on a SU-8 thin film layer. Reactive ion etching is appropriate for the large area pattern transfer with high aspect ratio pattern with appropriate RIE power and gas control. The glass etching rate and shape with various reactive ion etching conditions are reported for the nanoscopic patterns. This profile shows uniform pattern transfer in the large area substrate with fidelity. The proposed glass submicron patterning approach provides the advantages of both low cost and precise tailoring of submicron geometry, appropriate for mass production.

#### 4:00pm NS+NC-ThA7 STM Atom and Molecule Manipulation: Realizing Single Molecule Switches and Devices, S.-W. Hla, Ohio University INVITED

Scanning tunneling microscope (STM) manipulation of single atoms and molecules on surfaces allow construction of novel quantum structures on an atom-by-atom basis and demonstration of single molecule devices on a one molecule at-a-time basis. STM is not only an instrument used to '/see/' individual atoms by means of imaging, but also a tool used to '/touch/' and '/take/' atoms/molecules or to '/hear/' their vibration by manipulations. Therefore, it can be considered as the '/eyes', 'hands'/ and '/ears'/ of the scientists connecting our macroscopic world to the exciting atomic and nanoscopic world. In our research projects, we combine STM manipulation schemes with a variety of tunneling spectroscopy measurements to address several critical issues covering both fundamental understanding, and demonstration of novel atoms/molecules based nano-devices. In this talk, our recent results of single atom/molecule manipulations using a lowtemperature STM will be presented. The presentation will include atom manipulation on 3-D nanoclusters, comparative lateral force measurement to move individual atoms, manipulation of nanoscale bio-molecules to realize a multi-step single molecule switch, manipulation of Kondo effect in zero and two-dimensional molecular systems, and charge transfer molecular switching.

4:40pm NS+NC-ThA9 Nanopatterning of Functional Polymers by Thermal Dip-Pen Nanolithography, W.K. Lee, Naval Research Laboratory, W.P. King, University of Illinois, Urbana-Champaign, L.J. Whitman, National Institute of Standards and Technology, P.E. Sheehan, Naval Research Laboratory

Thermal dip-pen nanolithography (tDPN) uses a heated AFM cantilever coated with an ink to melt, deposit, and align the ink on a substrate.1 tDPN has proven particularly effective for depositing polymers.<sup>2,3</sup> The polymer thickness and lateral dimensions may be tuned by adjusting the tip heating power and the writing speed to allow layer-by-layer deposition. The deposited polymer is aligned along the writing direction apparently due to shear between the tip and substrate. Many different functional polymers have been successfully deposited on silicon oxide surfaces, including a temperature-responsive polymer [poly(N-isopropylacrylamide), known as pNIPAAM], a semiconducting polymer [poly(3-dodecylthiophene)], a piezoelectric polymer [poly(vinylidene fluoride)], and a light-emitting polymer [poly(9,9-dioctylfluorenyl-2,7-diyl)]. We will present our characterization of a deposited polymer. For example, pNIPAAM nanostructures by tDPN patterned in surface parallel form along the writing direction and undergo a hydrophilic-to-hydrophobic phase transition induced by temperature that allows the structures to controllably capture and release proteins.3 Moreover, we will demonstrate how a universal polymer carrier "ink" may be used to deposit a wide range of materials that could not be deposited under ordinary conditions. Finally, we will describe

the deposition and nanostructuring of aromatic molecules which may not be accessible by other scanning probe lithographic techniques.

<sup>1</sup> Sheehan et al., Appl. Phys. Lett., 85, 1589 (2004).

<sup>2</sup> Yang et al., J. Amer. Chem. Soc., 128, 6774 (2006).

<sup>3</sup> Lee et al., Soft Matters, accepted for publication (2008).

## 5:00pm NS+NC-ThA10 Selective Assembly of DNA-Templated Nanostructures for the Application to Nano-Device, *H.J. Kim, Y. Roh, B. Hong*, Sungkyunkwan University, Korea

The nanowires using the conjugation of DNA and metal (e.g., Ag, Au, Cu and Pd) are essential building blocks to realize the nanometer-scaled electronic devices and are being extensively investigated to apply to nanoscale electronic devices. However, there are remaining some problems for realization of DNA device such as fixing on specific location and aligning with uniform interval. We report an approach to selectively align and uniformly separate  $\lambda$ -DNA molecules and thus DNA-templaed gold nanowires (AuNWs) on SiO2 surface using surface-patterning technique by combination of self-assembly and conventional microfabrication processes. We also utilized the photolithography and plasma ashing methods to create molecular patterns comprised nano-scale patterned 3\_ (aminopropyl)triethoxysilane (APS) region and micron-scale octadecyltrichlorosilane (OTS) region that the key for highly selective assembly is the high-quality molecular layers. DNA was attached only on the APS region defined by the amine groups, but not on the surface of the OTS region. By surface-pattering technique, we could obtain DNA molecules and thus DNA-based AuNWs aligned parallel and selectively at 10 µm intervals on a Si substrate. We used atomic force microscopy (AFM) to analyze the configuration of AuNWs.

surface-pattering technique, plasma ashing,  $\lambda\text{-}\text{DNA}$  molecule, gold nanowires (AuNWs), APS, and OTS.

5:20pm NS+NC-ThA11 High Resolution STM Imaging and Manipulation of Multi-decker Porphyrin, *H. Tanaka*, Osaka University, Japan, *T. Ikeda*, Kyushu University, Japan, *M. Takeuchi*, NIMS, Japan, *S. Shinkai*, Kyushu University, Japan, *T. Kawai*, Osaka University, Japan

Supramolecular chemistry has emerged as a powerful strategy for construction of molecular-based devices with advanced functions and welldefined nanometer-scale structures. Structural determination of supramolecular aggregates is of great importance and mainly performed by means of NMR and/or X-ray crystal analysis. One of the convincing ways to evaluate or even visualize the structure, other than those just mentioned, is scanning probe microscopy. A large number of studies have been reported for ultrahigh vacuum scanning tunneling microscopy (UHVSTM) measurements of porphyrins, phthalocyanines, their mixtures, and covalently linked multi-porphyrins. In spite of submolecular/atomic resolution, the number of reports on high resolution UHVSTM images of supramolecules is still limited, due to the lack of suitable deposition method for such molecules without decomposition. We have overcome this difficulty by developing a pulse injection technique as a novel deposition method of fragile biomolecules, such as DNA/RNA/protein and supramolecules, such as porphyrin oligomers/macrocycles. Here we focus on the molecular system of multi-decker (double-decker(DD) and tripledecker(TD)) porphyrin on Au(111). The DD molecules are known to form highly ordered adlayers on HOPG. We have found that both DD and TD, deposited by pulse injection method, form highly ordered adlayers on Au(111). We also successfully observed rotation of topmost porphyrin of both DD and TD. To the best of our knowledge, there have been no reports of STM where such movement of "molecular bearing" (not rotation of entire molecular unit over the surface) has been detected in this way.

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