Nanometer-Scale Science and Technology
Room 210 - Session NS-WeA

Nanopatterning and Manipulation

Moderator: S.W. Pang, University of Michigan

2:00pm **NS-WeA1 Molecular Ruler Lithography Process with Sacrificial Multilayer Host Structures Incorporating a Barrier Layer**, ***S. Subramanian,*** *J.M. Catchmark,* Pennsylvania State University

Molecular ruler lithography has the potential of improving the achievable resolution of conventional lithography techniques, without resorting to new instrumentation. This is accomplished by scaling down the dimensions of functional host structure by selectively assembling organic molecules of precise length on their surface.@footnote1@ A novel method for performing molecular ruler lithography using sacrificial host structures has recently been developed and demonstrated using contact lithography.@footnote2@ This new approach provides a reproducible,high yield technique for selective removal of the host,fabricating high aspect ratio structures and isolation of the host material from the substrate. In order to make this process widely compatible with optical and electron beam lithography techniques, we introduce a modified molecular ruler lithography process using a sacrificial multilayer host structure which incorporates a barrier layer in between the sacrificial and the host material. This barrier layer prevents the lithography resist,developer and removal chemistries used to pattern the host material from interacting with the sacrificial material. We demonstrate this process by using contact lithographically patterned gold host structures to produce isolated platinum lines. The process consisted of depositing a sacrificial LOR resist (MicroChem) and a chrome barrier layer. A gold host feature was patterned on top of the chrome barrier layer using optical lithography. The chrome barrier was then selectively removed using reactive ion etching. Mercaptohexadeconoic acid molecules were assembled onto the patterned gold layer completing the fabrication of the sacrificial host structure. Platinum was then deposited and the host structure was selectively removed by dissolving the sacrificial LOR layer to leave behind the isolated platinum lines. @FootnoteText@ @footnote 1@Hatzor A, Weiss P, Science 291,1019. @footnote 2@Subramanian S, Catchmark J, JM3, accepted, 2005.

2:20pm **NS-WeA2 High Electric Field Nanoimprint Lithography of Metal Thin Films**, ***N. Farkas,*** *P. Meduri, E.A. Evans, R.D. Ramsier,* The University of Akron*; J.A. Dagata,* National Institute of Standards and Technology

Sputter-deposited ZrN thin films prepared with high nitrogen content exhibit superdiffusive scanning probe microscope (SPM) oxidation kinetics and oxide feature heights of several hundred nanometers. We extend this enhanced single-tip SPM oxidation to parallel writing with an inherently simple method to obtain large areas of submicrometer-scale oxide features on ZrN thin films. To investigate if this nanoimprint lithography technique can be used to create arrays of well-defined features on other metal surfaces, pattern transfer onto iron/iron nitride thin films is studied here. This comparison is of fundamental interest in that Zr oxidation is driven by oxygen migration, whereas Fe oxidizes by metal ion transport. Implication of the use of patterned Zr and Fe nitride thin films for biomedical and magnetic applications are also discussed.

2:40pm **NS-WeA3 Thermolithography for Micro- and Nanofabrication**, ***M.-T. Hung,*** *Y.S. Ju,* UCLA

An intriguing class of alternative lithography techniques utilize localized heating to create nanoscale features.@footnote 1@ The so-called thermolithography is very interesting since heat conduction in highly disordered polymer layers is a relatively slow diffusive phenomenon, which can be exploited to fabricate 3D nanostructures. We present our study of one type of thermolithography techniques that induces thermochemical cross-linking in select areas of a thin polymer layer. The patterned polymer layer can serve as part of a device or as a mask for subsequent processing. We demonstrate fabrication of T-gate structures and negative-slope resist profiles advantageous for the lift-off process. The thermal transport properties of polymer layers and kinetics of cross-linking processes are key parameters that determine the speed and resolution limit of the thermolithography techniques. We develop thermal transport property measurement techniques based on microfabricated ultra-thin membrane structures. The thermal conductivity and heat capacity of commercially available image reversal photoresists are determined before and after UV exposure, before and after postexposure bake, and also as a function of temperature. We also use micro-fabricated heaters coated with a polymer layer to induce precisely controlled heating and study kinetics of cross-linking. The spatial extent of cross-linking is determined by treating the polymer in a developer and examining the profile of the remaining layer using an SEM. The polymer profiles are compared with numerical heat conduction simulation results to extract the threshold cross-linking temperature as a function of heating duration. The present work demonstrates feasibility of a thermolithography technique and provides important data on the thermal transport properties and kinetics of polymerization that help guide further development of micro- and nano-scale thermolithography techniques. @FootnoteText@ @footnote 1@ A. S. Basu, S. McNamara, and Y.B. Gianchandani,J.Vacuum Sci. & Tech. B, 2004, 22, pp. 3217-3220. M. Kuwahara , J.H. Kim , J. Tominaga, Microelectronic Engineering, 2003, 67-68, pp. 651-656

3:00pm **NS-WeA4 Direct Deposition of Molecular Electronics Materials using Thermal DPN**, ***P.E. Sheehan,*** *M. Yang, A.R. Laracuente,* Naval Research Laboratory*; B.A. Nelson, W.P. King,* Georgia Tech*; L.J. Whitman,* Naval Research Laboratory

We have developed a new technique, called thermal DPN (tDPN),@footnote 1@ where a heated atomic force microscope cantilever controls the deposition of a solid "ink." The heated cantilever can be used like a nanoscale "soldering iron" or "glue gun" to deposit semiconductors, insulators, or metals. tDPN has several advantages over conventional DPN. Control over writing is much greater--deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. In addition, imaging with a cool tip does not appear to contaminate the surface, thereby allowing in situ confirmation of the deposited pattern. tDPN also expands the range of useable inks to those that are immobile at room temperature. Finally, multi-layer films can be deposited sequentially, enabling 3-D structures and heterostructures to be written directly. One material that is easily deposited by tDPN but which is challenging by other means is poly(3-dodecylthiophene), or PDDT. PDDT is a conducting polymer that shows great promise as an active component in organic electronic devices. Using tDPN, well-ordered PDDT nanostructures have been deposited on silicon oxide and gold surfaces with layer-by-layer thickness control. By adjusting the tip heating power and the writing speed, we can vary the polymer thickness from a single monolayer (~2.6 nm) to tens of monolayers with lateral dimensions below 100 nm. Unlike conventional DPN inks, this low vapor pressure polymer may be deposited in UHV by tDPN, thereby allowing integration with CMOS processing. Along with our success at depositing metallic indium nanowires via tDPN, we now have all the requisite elements for the direct deposition of electronic circuitry. @FootnoteText@ @footnote 1@ P. E. Sheehan, L. J. Whitman, W. P. King, B. A. Nelson, Appl. Phys. Lett. 85, 1589 (2004).

3:20pm **NS-WeA5 Physical Processes in Atom Manipulation and Creation of Novel Nanostructures of Co and Cu Atoms on Cu(111) Surfaces***, ***J.A. Stroscio,*** *R.J. Celotta,* NIST **INVITED**

We are studying the interactions involved in STM atom manipulation using Co and Cu atoms on a Cu(111) surface@footnote 1@ and building novel CoCu nanostructures using atom manipulation. The interactions responsible for atom manipulation are investigated by measuring the atom dynamics with a STM using both imaging and tunneling spectroscopy methods. Manipulated atom imaging, where the manipulated atom is rastered in the trapping potential of the STM tip, reveals the binding sites of the substrate. Contrast in this new type of image is due to the tip sensing the presence of the adatom, which can reflect atom motion and a variation in the local potential energy surface. Quantitative measurements of atom dynamics are made by studying the tunneling current noise properties during atom manipulation. Two distinct mechanisms of atom motion can be identified in the noise dynamics; quantum tunneling of the adatom between neighboring lattice sites, and vibrational heating of the adatom by inelastic electron scattering. The magnetic Co atom is a Kondo impurity on Cu(111) surfaces at low temperatures. The interaction between Co and Cu can be tuned by varying the Cu coordination in nanostructures built by atom manipulation. These nanostructures show significant changes in the Kondo density of states resonance as a function of Cu coordination. *This work is supported in part by the Office of Naval Research. @FootnoteText@@footnote 1@J. A. Stroscio and R. J. Celotta, Science 306, 242 (2004).

4:00pm **NS-WeA7 Chemically Engineering the Motion of Individual Molecules on the Si(100)-2x1 Surface: a Scanning Tunneling Microscopy Study**, ***R. Basu***, *J.D. Tovar, M.C. Hersam,* Northwestern University

Room temperature ultra-high vacuum (UHV) scanning tunneling microscopy (STM) is used to study a unique bond-breaking mediated motion of individual organic molecules on the clean Si(100)-2x1 surface. Specifically 4-methoxystyrene molecules are observed to undergo switching between two cycloaddition conformations mediated by pivotal motion about one Si-C bond. Styrene molecules, on the other hand, do not undergo such lateral translations, thus suggesting that the rotational degree of freedom of the methoxy group is responsible for the apparent motion of 4-methoxystyrene. To test this hypothesis, the rotational degree of freedom of the methoxy group was suppressed by synthesizing an analog molecule (5-vinyl-2,3-dihydrobenzofuran) where the methoxy group is covalently linked back to the aromatic ring. UHV STM imaging of 5-vinyl-2,3-dihydrobenzofuran on clean Si(100)-2x1 indeed confirms the suppression of molecular motion. This study suggests that the motion of organosilicon adsorbates can be controlled by chemically engineering their intramolecular degrees of freedom.

4:20pm **NS-WeA8 Formation of Large-Area Nanostructures on Si and Ge Surfaces during Low-Energy Ion Beam Erosion**, ***B. Ziberi***, *F. Frost, B. Rauschenbach,* Leibniz-Institut für Oberflächenmodifizierung e.V. Leipzig, Germany

In contrast to advanced lithographic methods and subsequent etching procedures for pattern production with structure size < 100 nm, which are complex technological processes, self-organized spontaneous pattern formation during low-energy ion beam erosion is a cost-efficient `bottom up` approach for the fabrication of large-area nanostructures. The formation of these patterns can be observed on various semiconductor materials and is attributed to a surface instability between curvature dependent sputtering that roughens the surface and smoothing by different surface relaxation mechanisms. In these work results for pattern formation due to low-energy noble gas (Ne@super +@, Ar@super +@, Kr@super +@, Xe@super +@) ion beam erosion of silicon and germanium surfaces at oblique ion incidence with and without sample rotation are presented. Depending on ion beam parameters, i. e. ion energy, ion incidence angle and ion mass, different patterns can evolve on the surface. In the case with sample rotation, very well ordered dot structures evolve on the Si surface at glancing incidence angle of 75° with respect to surface normal, with size varying from 30 nm to 50 nm. Without sample rotation, at small ion incidence angles, remarkably high ordered ripple patterns with wavelength ~ 50 nm can form on both materials for similar sputtering conditions. By further increasing the ion incidence angle a transition from ripples to highly hexagonally ordered dot structures with periodicity of ~ 40 nm are observed. The lateral ordering of nanostructures increases with erosion time, leading to very well ordered and homogenous structures. The mean size of nanostructures can be adjusted with ion energy while maintaining their lateral ordering. Scanning force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) were used to study the lateral ordering, shape, and size of these nanostructures.

4:40pm **NS-WeA9 Thermally Assisted Atom Transfer on Surfaces: Between Tunneling and Activated Diffusion**, ***J.W. Gadzuk***, NIST

The low temperature rates for site-to-site transfer of single atoms and molecules adsorbed on surfaces have been determined in recent STM studies@footnote 1@ within the temperature regime where the dominant transfer mechanism changes from mostly activated transmission over to thermally assisted tunneling through the inter-site (transition state) barrier, as the temperature is reduced. A model that has provided useful conceptual and quantitative insights into thermally assisted field emission tunneling spectroscopy@footnote 2@ is used here as the basis for theory of site-to-site atom transfer in this temperature range where proper account of tunneling and quantum reflection, for energies below and above the transition state barrier is required. The predicted transfer rates which are very sensitive to barrier shape as well as height, agree well with those observed in the STM studies of Co and Cu on Cu(111) surfaces in the interesting 4K@<=@T@<=@7K transition range which is relevant in the atom-by-atom fabrication of thermally stable surface nanostructures. @FootnoteText@ @footnote 1@J. Repp, G. Meyer, K.-H. Rieder, and P. Hyldgaard, Phys. Rev. Letters, Vol.91, 206102 (2003); J. A. Stroscio and R. J. Celotta, Science, Vol.306, 242 (2004).@footnote 2@J. W. Gadzuk and E. W. Plummer, Phys.Rev.B Vol.3, 2125 (1971).

5:00pm **NS-WeA10 Patterning of Well-Ordered PZT Nanodot Arrays using Silicon Nitride Shadow Mask**, ***H.-J. Shin***, *J.H. Choi, H. Yang, Y.D. Park, Y. Kuk,* Seoul National University, Korea*; C.J. Kang,* Myungji University, Korea

We patterned well ordered arrays of Pb(Zr@sub 0.2@Ti@sub 0.8@)O@sub 3@ nanodots on a SrRuO@sub 3@/SrTiO@sub 3@ substrate by pulsed laser deposition. A silicon nitride shadow mask with ordered holes was used for patterning of PZT arrays. This method have an advantage that deposition could be done at high temperature, which could be applicable to in situ deposition avoiding any possible contamination in dot formation. In addition, we could change the shape or size of the patterns if necessary. The SrRuO@sub 3@ bottom electrode and PZT nanodots were deposited at 760 @super o@C and 660 @super o@C, respectively. The lateral size of the dot was about 120 nm and the height was about 15 ~ 20 nm. The inter-dot distance of PZT dot arrays was about 200 nm, exactly the same as the pore-to-pore distance of the shadow mask. Each dot was fully arranged and well isolated, having dome shape after deposition. The local switching of a single dot was examined using piezoresponce force microcopy. We could observe that the absolute piezoresponse value of positively polarized dot is 28.3 % larger than that of negatively polarized background, and there weren't any noticeable inhomogeneity such as an inversion of center region after polarization. The polarized states were maintained at 61.3 % of initial value after ~ 20 min, which almost relaxed suddenly to noise level after 30 min. A sudden drop of polarization implies that the relaxation is mainly related to the nucleation stages of domain reversal in our case.

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