Thursday Morning, November 5, 1998

Nanometer-scale Science and Technology Division
Room 321/322/323 - Session NS-ThM

Nanoscale Patterning and Modification

Moderator: J.F. Wendelken, Oak Ridge National Laboratory

8:20am **NS-ThM1 Fabrication of Nanometer Size Photoresist Wire Patterns with a Silver Nanocrystal Shadowmask*, S. Choi*,** *K.L. Wang,* University of California, Los Angeles*; M. Leung, G. Stupian, N. Presser,* The Aerospace Corporation*; S. Chung, G. Markovich, S. Kim, J.R. Heath,* University of California, Los Angeles

We propose a new method of fabricating precisely defined nanometer size photoresist wire patterns by exposing electron beams onto silver(Ag) nanocrystal wires which have already been deposited on photoresist film. Ag nanocrystals linked with organic ligands were fabricated first using an organically functionalized Ag nanocrystal technique. Arrays of high aspect ratio wires formed spontaneously at the air/water interface when these Ag nanocrystals were dropped onto water. Ag nanocrystal wire structures were then transferred onto the polymethyl methacrylate(PMMA) coated substrates by the Langmuir-Blodgett lift-off process. To prepare a thick Ag nanocrystal shadowmask, a second monolayer of Ag nanocrystal wires was added to the previously deposited monolayer. The occupied areas by organic ligands between the nanocrystals in the wire decreased through a metallization process in air. Monte Carlo simulation was done to estimate the electron stopping effectiveness for the Ag nanocrystal shadowmask at low voltages. Low energy electron beam exposure resulted in numerous 50nm wide wire patterns on photoresist film. The wire patterns were defined in the photoresist material by spatially selective electron beam exposure on the Ag nanocrystal wire shadowmask. The wire patterns on photoresist film can be used for pattern transfer to many different substrates by subsequent selective etching for use in device fabrication. Our new method therefore enables rapid and low cost fabrication of quantum wire structures.

8:40am **NS-ThM2 Fabrication and Structuring of Ordered Two-Dimensional Nanopore Arrays in Anodic Alumina*, A.P. Li*,** *F. Mueller, A. Birner, K. Nielsch, U.M. Goesele,* Max-Planck-Institute of Microstructure Physics, Germany

We will describe the fabrication of nonlithographic nanopore arrays in anodic alumina with areal pore densities in the 6*10@super 8@ - 5*10 @super 10@ cm @super -2@ range, and the lithographic structuring of the arrays for potential applications in photonic crystal. A two-step anodization process was used to oxidize aluminum in oxalic, sulfuric, and phosphoric acid solutions. Self-organized hexagonal pore arrangements were formed in the end of the first anodization process. After removing the irregular upper part, the densely ordered pits in the bottom of anodic layer act as natural masks, and the nanopore arrays were fabricated by the second anodization process. Perfect ordered pore arrays were obtained within domains of a few micrometers, which are separated from neighboring domains with different orientation of the pore lattice by grain boundaries, i.e., the nanopore arrays show polycrystalline structure. The pore distance can be controlled by changing the anodic electrolyte and voltage. The ratio of pore diameter and wall thickness can be adjusted by chemical etching after anodization. The structural characteristics make the ordered porous alumina a potential two-dimensional photonic crystal material for the visible to ultra-violet light range. Although they are polycrystalline, these structures are expected to exhibit interesting photonic crystal properties analogous to electronic properties of polycrystalline semiconductors. For optical transmission measurements, light has to be coupled in perpendicular to the pore arrays and to traverse a well defined number of pore layers. For this purpose we have developed a lateral structuring technique that allows to remove the porous alumina precisely yielding vertical walls. Bars of porous alumina which are 100-400 µm wide, 100-300 µm high and several mm long have been prepared. The achieved samples are well suited to investigate the optical properties of these structures with light traveling perpendicular to the pore arrays.

9:00am **NS-ThM3 Chemically Assisted Ion-Beam Etching of Submicrometer Features in GaSb-based Quantum Wells*, G. Nagy*,** *R.U. Ahmad, M. Levy, R.M. Osgood, Jr.,* Columbia University*; M.J. Manfra, G.W. Turner,* Massachusetts Institute of Technology

GaSb-based semiconductor systems are of interest because of their potential applications in advanced microelectronic and optical devices. For example, GaSb-based materials have been used for the fabrication of resonant interband tunneling devices, as well as high performance laser diodes, and midinfrared photodetectors. Anisotropic, high-resolution dry etching is a desirable processing technology for device fabrication in this semiconductor system. Here, we have used electron beam patterning and chemically assisted ion beam etching to fabricate structures down to 200 nm in diameter in GaSb and in GaInAsSb/AlGaAsSb multiple quantum well material. The chemically assisted ion beam etching was performed with chlorine as the reactive gas and Ar@super +@ ions of 400-900 eV energy. With the GaSb substrate, the Cr masks used to fabricate the features exhibited good etch selectivity and smooth, highly anisotropic structures were realized. The measured etch rates of GaSb were successfully fitted to a model of chlorine-based chemically assisted ion beam etching that assumes the formation and desorption of trichloride etch product species. With the GaInAsSb/AlGaAsSb multiple quantum well material, the chemically assisted ion beam etching provided highly anisotropic pattern transfer using Cr as the mask material. Efforts are underway to examine the dependence of etch damage on incident ion energy for 200-1000 nm diameter features in the multiple quantum well material using photoluminescence spectroscopy at 4K.

9:20am **NS-ThM4 Nanometer-scale Sputter-Induced Rippling of the SiO@sub2@ Surface Characterized with Real-Time X-ray Scattering*, C.C. Umbach*,** Cornell University*; R.L. Headrick,* Cornell High Energy Synchrotron Source*; B.H. Cooper, J.M. Blakely,* Cornell University*; E. Chason,* Sandia National Laboratories

Certain advanced technologies (quantum wires, dots, etc.) may require surfaces with periodic topographic modifications to produce desirable length scales during fabrication. The formation of ripples on the surfaces of materials during ion sputtering has been known for decades and represents a potentially useful type of periodically modified substrate. In this paper we report on forming ripples on thermally-grown SiO@sub 2@ while the structure of the ripples is monitored in real-time with x-ray scattering. Ripples were formed in UHV using argon ions with energies between 0.5 and 2 keV. Ripple wavelengths between ~150 and ~600 Å were formed, with the wavelength increasing linearly with the ion energy. During sputtering, both the specular and diffuse intensity of 11 keV x-rays scattered from the surface were measured. Well-defined peaks in the diffuse scattering allow the determination of the ripple morphology. The effects of annealing during or after sputtering can also be monitored. Real-time monitoring of the ripples may permit more precise control of aspects of the ripple structure. The mechanism of ripple formation will be discussed in the context of theories of surface instabilities associated with ion bombardment.

9:40am **NS-ThM5 Materials Considerations for Optical Lithography at the Nanometer Scale*, F.A. Houle*,** *W.D. Hinsberg, M.I. Sanchez, J. Hoffnagle, M. Morrison, C. Nguyen,* IBM Almaden Research Center

The extendability of polymeric photoresist systems to the fabrication of nanostructures is a critical issue for both conventional microelectronics and for new device concepts. We have developed techniques using deep-UV interferometric lithography to evaluate quantitatively the relationship between polymer properties and reactivity and structure formation, with a particular focus on chemically amplified resist systems. Extended grating structures ranging from 50 to 500 nm linewidth and millimeters of line length are readily produced using 257 nm light, enabling systematic studies of the scaling of both chemical and physical phenomena. The apparatus and experimental methods will be described. We will present data using real-time spectroscopy and AFM analyses that probe the role of acid diffusion and aerial image definition in determining dimensional control and line-edge roughness at the nanometer scale. Implications of the data for x-ray and electron-beam resists will be discussed.

10:00am **NS-ThM6 Nanofabrication of Organic Thin Film Materials Using Scanning Probe Lithography*, G. Liu*,** *S. Xu, K. Wadu-Mesthrige, Y. Qian,* Wayne State University

Scanning probe microscopy(SPM) allows the surface structure to be visualized with unprecedented spatial resolution. Under carefully chosen conditions, SPM tips or probes can be used as a manipulation tool to fabricate nanoscopic patterns on surfaces. Recent work in our laboratory focuses on using SPM tips to fabricate nanopatterns on the surfaces of organic thin films. The talk will describe two new techniques developed in our lab. First method is nanografting which utilizes atomic force microscopy (AFM) tips as a nanoshaver. Such a shaver is operated on a self-assembled monolayer matrix in a solution containing adsorbate molecules. New molecules adsorb onto the shaved area following the plowing track of the AFM tip. Second methods utilizes scanning tunneling microscopy (STM) tips which operates under a high tunneling current. Single layers of metals can be removed from desired locations. The advantage and potential applications of the two techniques will also be discussed.

10:20am **NS-ThM7 Proximity X-ray Lithography of Siloxane and Polymer Films Containing Benzyl Chloride Functional Groups***, **S.L. Brandow**, W.J. Dressick, C.S. Dulcey,* Naval Research Laboratory*; H. Witschi, P.F. Nealey,* University of Wisconsin

Siloxane and polymer films containing benzyl chloride functional groups were exposed to patterned proximity x-rays. Silicon wafers coated with films of (p-chloromethyl)phenyl-trichlorosilane (CMPTS) or spun coated poly-vinyl benzyl chloride (PVBC) were exposed at the University of Wisconsin synchrotron x-ray source using 0.9385 nm radiation (800 MeV) at doses ranging from 50-1500 mJ/cm@super2@. Exposure resulted in changes to the surface energy and chemical reactivity of the imaging layers. The loss of chlorine and formation of oxidized carbon photoproducts upon exposure was followed as a function of dose using x-ray photoelectron spectroscopy. A corresponding change in surface energy, as monitored by static water contact angle, was also observed. The successful chemical grafting of amine ligands to the portions of the siloxane and polymer films which have been exposed to proximity x-rays definitively establishes the formation of surface aldehyde or ketone groups as a major photochemical pathway. The resulting surface amine was used to covalently bind either a fluorescent tag or a colloidal Pd(II) nanoparticle capable of initiating the deposition of electroless Ni. Pattern formation is demonstrated and the mechanistic differences of photoproduct formation on siloxane and polymer films will be discussed.

10:40am **NS-ThM8 Nanofabrication of Apertures for Single Quantum Dot Spectroscopy***, D. Park, **C.R.K. Marrian**, D. Gammon, R. Bass, P. Isaacson, E. Snow,* Naval Research Laboratory

Optical spectroscopy of quantum dots can be performed by probing sub micron lateral regions of a quantum well through apertures in an opaque metallic film on the surface of a sample. The apertures must be small, smooth to avoid scattering the incident light and fabricated without inducing damage in the quantum well, i.e. without an etch process. We have developed a technique based on a metal lift-off using electron beam nanolithography in a negative resist. (The resist is patterned, developed, coated with metal film and then treated with a solvent to remove the remaining resist to lift-off the metal in areas where it covers the resist.) The use of a positive resist (the preferred choice for lift-off) would require prohibitively long write times as the entire sample except the apertures would have to be exposed. Obtaining the undercut (e.g. re-entrant) profile required to form a clean edged lift-off is difficult with negative beam resists. However, using 20 kV electrons, an undercut profile can be obtained by using a sufficiently thick (>1 µm) resist layer. To obtain sub 200 nm apertures, we have used our 50 kV e-beam tool. However, it is not possible to obtain an undercut profile directly with 50 kV electrons as even a thick resist film does not stop a sufficient number of the incident electrons as occurs at 20 kV. By changing to an area, as opposed to a point, exposure high aspect ratio (~10:1) resist features with vertical sidewalls can be obtained at 50 kV. An oxygen plasma treatment has been found to smooth the sidewalls of the resist features and to provide a slight undercut sufficient to give a clean aperture following metal lift-off. These lithographic results will be compared to, and shown to be in quantitative agreement with, the predictions of our simulations of electron elastic and inelastic scattering. Finally, an example of the spectroscopy will be presented along with a discussion of the relative advantages of this technique over spectroscopy with a near field probe.

11:00am **NS-ThM9 Nanolithography and Macromolecular PMMA***, **E.A. Dobisz**, S.L. Brandow, R. Bass, L.M. Shirey,* Naval Research Laboratory

Polymethylmethacrylate (PMMA) has been the standard high resolution resist for over 20 years. The limits to its resolution has been the subject of many controversies that center upon our understanding of e-beam interactions with materials over 10 nm length scales, resist development, and the utility of macromolecular resists for very high resolution lithography. In this work nanolithographic pattern development is examined from the latent image formation through the evolution of surface morphology as patterns develop. Two molecular weights of PMMA, 950K and 50K were spun onto Si wafers as 50 nm thick films. Lithographic patterns consisted of: (1) large (1-20 mm) pads with a 50 nm gap of exposure in the center and (2) grating patterns of 10 nm lines on periods from 40-100 nm to examine the limit of the resist material on pattern density. Exposures were made by 50 kV e-beam lithography system with a Gaussian probe standard deviation of 8 nm. The resist patterns were examined by AFM operated in tapping and contact modes. Examination of as-baked PMMA showed a nodular structure, with average particle diameters of 50 nm. Morphological changes during development will be discussed. AFM latent images of detected e-beam exposure show a 0.2-2.9 nm depression in the resist. Latent images are observed over a much larger dose latitude than observed in developed patterns. In developed grating patterns the 60 nm period is critical. The granular structure of 50K resist prevented the development of the 60 nm grating. In the 950K resist, the 60 nm grating developed readily, but the 40 nm period grating is problematic. AFM images show etching of the particle boundaries across the resist between the lines to prevent formation of the 40 nm grating. AFM images are compared and contrasted to SEM micrographs. The results are discussed in terms of electron scattering during exposure, resist contrast, stress, and resist structure.

11:20am **NS-ThM10 Indium Phosphide Nanocrystals formed by Sequential Ion Implantation into Fused Silica***, D.O. Henderson, R. Mu, A. Ueda, M.H. Wu, **D. Denmark**,* Fisk University*; C.W. White, A. Meldrum, R.A. Zuhr,* Oak Ridge National Laboratory

Indium followed by phosphorous were implanted into optical grade fused silica at energies of 320 and 120 keV, respectively and at doses ranging from 1x10@super 16@ ions/cm@super 2@ to 1x10@super 17@ ions/cm@super 2@. The implanted substrates were annealed at 800°C for 1 h in a reducing atmosphere (5% H@sub 2@ +95% Ar). Vibrational and electronic spectra were recorded before and after annealing the samples. The vibrational spectra revealed a peak at 320 cm@super -1@ after annealing at 800°C. The intensity of this peak increased with ion dose and is assigned to the surface phonon of InP nanocrystals. XRD measurements confirmed the presence of crystalline InP and TEM showed particles with radii ranging from 4.6 to 11.6 nm. Electronic spectra of the annealed samples indicated that the energy of the band edge absorption is well below the bulk value of 969 nm. The band gap energies increased with decreasing ion dose and is attributed to quantum confinement of the exciton. The quantum confinement of the exciton is supported by the TEM measurements which demonstrated that the nanocrystals are nearly equal to or smaller than the InP exciton radius of 10.7 nm.

Author Index

Bold page numbers indicate presenter