Wednesday Afternoon, October 30, 2013

Nanometer-scale Science and Technology
Room: 203 B - Session NS+BI+EM-WeA

Nanopatterning and Nanolithography
Moderator: P.E. Sheehan, Naval Research Laboratory

2:20pm NS+BI+EM-WeA2 Tunneling Electron Induced Adsorption of Copper Phthalocyanine on the Cu(111) Surface, *T. Stock**, *J. Nogami*, University of Toronto, Canada
The adsorption of up to one monolayer (ML) of copper phthalocyanine (CuPc) molecules on a room temperature Cu(111) surface has been studied using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Below 1 ML the molecules are in a fluid state and are highly mobile on the surface. At 1 ML coverage the molecules coalesce into a highly ordered 2D crystal phase. At sub-ML coverages, adsorption of individual CuPc molecules can be induced through exposure to tunneling electrons at a bias voltage exceeding a threshold value . This tunneling electron induced adsorption effect allows for a novel variety of molecular STM lithography, and permits probing of the mechanisms involved in the adsorption of individual molecules.

2:40pm NS+BI+EM-WeA3 STM Study of Pyramid Structures on Ge(110) Formed by Argon Ion Sputtering, *M.S. van Zijll, S. MacIntyre, S. Chiang*, University of California, Davis
Defects often act as nucleation points for island growth on surfaces. Earlier studies found that sputtering surfaces of silicon and germanium could create ordered arrays of dot and ripple structures. As a result of the sputtering and annealing cleaning procedures on Ge(110), we had previously observed the formation of pyramid structures, which could serve as engineered defects for island growth. Although these structures had some similarities to the dot patterns observed by other groups, the better defined shapes and the larger separation between the pyramid structures were striking. In an effort to better understand and control the formation of these defects, we used scanning tunneling microscopy (STM) under ultra high vacuum (UHV) conditions to measure the shapes, sizes, and spatial distribution of the observed pyramid structures on Ge(110) as a function of the argon ion sputtering energy. The samples were sputtered with low-energy ions ranging from 200eV to 500eV at an incident angle of 34°. The bases of the pyramids are rhombuses due to the 16x2 reconstruction of the Ge(110) surface. The lengths of the rhombuses range from 10 to 80nm, and the side-walls slant upward at ~4° from the horizontal. A Monte Carlo simulation of the sputtering process is used to determine the dependence of the sputtering yield on the binding energy of the surface atoms and on the incident ion energy, thereby giving insight into the process of pyramid formation.

3:00pm NS+BI+EM-WeA4 Enhanced Electrical Conductivity by Au Nanoparticle Islands Deposited from Solution, *F. Jiang, A.J. Muscat*, University of Arizona
Colloidal Au nanoparticles (NPs) capped with tetraoctylammonium bromide (TOAB) were synthesized using the Brust method, and deposited on oxidized p-type Si(100) covered by either 3-aminopropyltrimethoxysilane (APTMS) or 3-mercaptopropyltrimethoxysilane (MPTMS). Dip coating was used to deposit the Au NPs with nominal diameters of 5-20 nm using the linker 1,2-ethanedithiol (EDT). One coating cycle consisted of immersion in the Au NP colloid for 1 h, rinsing in toluene, immersion in EDT for 1 h, and rinsing in toluene. Deposits were made of one half-cycle (NPs only) up to 9 complete cycles. After deposition the samples were annealed for 1 h at 300°C in flowing N$_2$, which removed at least 85% of the organic compounds based on FTIR. SEM and cross-sectional TEM showed that after 9 cycles, 40% of the surface was covered with small islands consisting of clusters of Au NPs that were 10-20 nm in diameter and 20-30 nm apart from one another. AFM showed that the heights of the islands were also 20-30 nm. FTIR also showed that EDT replaced only half of the TOAB on the surface, suggesting that island growth is caused by TOAB ligands blocking binding sites. Current-voltage (IV) measurements were made by clamping two Cu terminals with a contact area of 6 mm^2 to the surface of a sample, separated by a distance of 10 mm. The film stack consisted of a) p-type Si substrate, b) 1.6 nm silicon oxide layer, c) 0.7-3 nm silane layer, and d) Au islands. A control experiment in which the Au NP islands were replaced by two 20 nm thick e-beam deposited Au films separated by a 10 mm gap yielded a sigmoidal IV curve due to current flow through the p-type Si substrate and possibly to lateral charge transfer through the APTMS monolayer. The Au NP islands increased the current flow at negative bias relative to the control. The Au NP islands could reduce the contact resistance or electrons could hop or tunnel between islands, through the underlying silane layer. Compared to the nanometer scale 1D Au NP arrays on BNNTs reported in the literature, electron transfer over such a large area found in this study could be used to scale up the class of semiconductor-free transistors that operate based on electron tunneling and could contribute to other applications that require effective local charge transfer, such as the seed layer for electro- and electroless deposition.

4:00pm NS+BI+EM-WeA7 Nanoimprinted Amorphous Metals for Energy Applications, *J. Schroers, A.D. Taylor, R.C. Sekol,* Yale University, *G. Doubek,* IPEN, Brazil, *G. Kumar,* Texas Tech University, *M. Carmo,* Forschungszentrum Jülich GmbH, Germany, *F. Gittleson, N. Hardesty-Dyck,* Yale University, *S. Mukherjee*, University of North Texas
INVITED
Here we report a unique CMOS compatible approach using bulk metallic glass Pt$_{58}$Cu$_{15}$Ni$_5$P$_{22}$ (Pt-BMG) [1] to create high performance fuel cell catalysts. We have shown that these materials can be nanoimprinted into ~10 nm diameter rods with aspect ratio up to 200 [2]. A nanoporous Al$_2$O$_3$ was used as a template to create the nanorod surface. The Pt-BMG is heated into the supercooled liquid region where it softens and can be thermoplastically imprinted. Under an applied pressure (ca. 50 MPa) the Pt-BMG fills the nanopores. An additional step can separate the nanorods from the reservoir [3]. The uniformly vertical nanorods are well-isolated and parallel to one another.

Our results show that these materials are highly active with lower onset potentials for CO, methanol, and ethanol oxidation [4]. In this talk we will demonstrate how these BMG systems can also serve as a platform for stategically designed catalyst systems. As a proof of concept we have modified the surface of a Pt-BMG by depositing ruthenium using underpotential deposition. We show that this approach facilitates the fabrication of multicomponent nanowires having elements outside of the glass formability with enhanced methanol oxidation beyond the initial Pt-BMG.

References:

1. Schroers, J. and W.L. Johnson, *Highly processable bulk metallic glass-forming alloys in the Pt-Co-Ni-Cu-P system.* Applied Physics Letters, 2004. **84**(18): p. 3666-3668.

2. Kumar, G., H.X. Tang, and J. Schroers, *Nanomoulding with amorphous metals.* Nature, 2009. **457**(7231): p. 868-872.

3. Schroers, J., Q. Pham, and A. Desai, *Thermoplastic forming of bulk metallic glass - A technology for MEMS and microstructure fabrication.* Journal of Microelectromechanical Systems, 2007. **16**(2): p. 240-247.

4. Carmo, M., et al., Bulk Metallic Glass Nanowire Architecture for Electrochemical Applications. Acs Nano, 2011. **5**(4): p. 2979-2983.

4:40pm NS+BI+EM-WeA9 Submicron Cylindrical Gratings for Rotation Sensors, *J. Laukkanen*, University of Eastern Finland, *S. Tonchev, Y. Jourlin, S. Reynaud,* CNRS, France, *H. Hirshy, S.G. Scholz,* Cardiff University, UK, *O. Parriaux*, CNRS, France
We demonstrate a production chain for making submicron gratings on the wall of a cylinder. Gratings of this kind can be used, for example, in rotation sensors. We have converted a conventional 2D interference lithography setup into 3D setup by using a circularly symmetrical planar high index phase mask [1]. With this method, a lot smaller period is achieved than with CNC tools, which are commonly used for similar structures.

A planar phase mask was made in CVD-grown silicon nitride (Si$_3$N$_4$) on top of a quartz mask plate using electron beam lithography and reactive ion etching. Silicon nitride was chosen as a grating material because of its high refractive index and therefore ability to cancel zeroth order transmission [2]. In photolithography, a specially made glass cylinder was used as a substrate and it was coated with photoresist by dip coating. The phase mask was illuminated with radially polarized light in oblique incidence creating an interferogram on the resist coated wall of a cylinder. The produced stitchingless grating lines were over one millimeter long.

In order to be able to mass produce these cylindrical gratings a nickel mold was done using electroforming like in LIGA process [3]. The nickel mold can then be used in injection molding. With this fabrication method, we can control the exact number of lines and spaces and have a constant period over the whole round of the cylinder, which is crucial for high precision rotation sensors.

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* NSTD Student Award Finalist

[1] S. Tonchev, Y. Jourlin, C. Veillas, S. Reynaud, N. Lyndin, O. Parriaux, J. Laukkanen, and M. Kuittinen," Subwavelength cylindrical grating by holistic phase-mask coordinate transform," *Optics Express*, **20**, 7946-7953 (2012).

[2] E. Gamet, A. V. Tishchenko, and O. Parriaux, "Cancellation of the zeroth order in a phase mask by mode interplay in a high index contrast binary grating," *Applied Optics*, **46**, 6719–6726 (2007).

[3] W. Bacher, W. Menz, J. Mohr, "The LIGA technique and its potential for microsystems-a survey," *Industrial Electronics, IEEE Transactions on*, **42**, 431 (1995).

5:00pm NS+BI+EM-WeA10 DNA Assembly on Nanopatterns Created by Electron Beam Lithography, *A.K. Pradhan*, Norfolk State University

A major goal of nanotechnology is to couple the self-assembly (SAMs) of molecular nanostructures with conventional micro as well as nanofabrication, for instance the so-called bottom-up and top-down fabrication methods would enable us to register and recognize individual molecular nanostructures in order to integrate them electronically into functional devices. However, the integration of top-down (lithographic pattern) with bottom-up (functionalizing with synthetic chemical) approaches remains a central challenge in nanofabrication. We demonstrate that the selective self-assembly of DNA nanostructures can happen on electron beam lithographically patterned surfaces at lower energy. The fluorescent dye coupled amine modified DNA nanostructures were selectively attached to the patterned glass substrates. The optimized binding interaction between self-assembled DNA nanostructures occurred preferably at lower beam energy due to the attractive energy between the pattern and DNAs . Patterns containing self-assembled DNA molecules with dimensions as small as 2 nm in height and 68 nm in width have been successfully demonstrated. The periodicity in DNA self-assembly was observed. This technology of combination of "top-down" fabrication and "bottom-up" self-assembly may find use wherever there is a need to attach self-assembled DNA molecules in a nanometer scale patterned surface for various applications.

5:20pm NS+BI+EM-WeA11 Organic Resist Materials for sub-20 nm Patterning: Robust Materials Enabled by Crosslinking Based Designs, *C. Henderson, R. Lawson, A. Cheshmekhani*, Georgia Institute of Technology

Future scaling of integrated circuits (IC) is in jeopardy due to a number of challenges related to both future material and process requirements that are needed to allow for fabrication of sub-20 nm IC devices. One of the most critical challenges is that of developing patterning technologies that can allow for formation of sub-20 nm patterned structures in a fast and economically viable manner. Extreme Ultraviolet Lithography (EUVL) is poised to be the successor to current 193 nm optical lithography for high volume manufacturing (HVM) of integrated circuits. However, problems in developing sufficiently bright exposure sources for EUVL have hindered its ramp into HVM. Now that source power difficulties appear to be on a path to being addressed, the other critical problem of developing resist materials that are capable of being patterned with EUV radiation and which can produce the desired sub-20 nm patterned features must be addressed. Current chemically amplified resist material designs will be incapable of satisfying all of the patterning requirements for EUVL, and this alternative resist material designs will be needed to enable successful integration of EUVL.

The goal of our work has been to develop novel organic resist materials that can enable sub-20nm patterning using EUVL. One of the critical challenges for producing sub-20 nm organic material patterns is that conventional positive tone polymeric resists exhibit poor mechanical stability at such dimensions and are thus prone to pattern collapse during development and drying. Furthermore, photoacid diffusion in conventional positive chemically amplified resists limits their resolution. As a result, one of our design strategies has been to explore the use of molecular resists that can either be crosslinked upon to exposure to operate in a negative tone manner or which can be crosslinked and depolymerizes upon exposure to operate in a positive tone fashion. We will present our latest results on these two families of materials and will show examples of organic resists that are capable of resolving 10 nm features using 100 keV e-beam lithography and sub-20 nm features using EUVL. The detailed materials design and mechanisms underlying these capabilities will be discussed.

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