

Monday Afternoon, October 29, 2012

Nanometer-scale Science and Technology

Room: 12 - Session NS+SP-MoA

Nanopatterning and Nanolithography

Moderator: P.E. Sheehan, U.S. Naval Research Laboratory

2:00pm **NS+SP-MoA1 Optical Properties of As-Prepared and Annealed Gold Nanostructures Fabricated by Interference Lithography**, *A.B. Tsargorodskaya*, University of Sheffield, UK, *A.V. Nabok*, Sheffield Hallam University, UK, *A.J. Lee*, University of Leeds, UK, *G.J. Legget*, University of Sheffield, UK

Gold nanostructures were fabricated by interferometric lithography (IL) with a view to their application for optical bio-sensing based on localized surface plasmon resonance. This approach relies upon very modest instrumentation, high processing speed and capacity for fabrication of dense arrays of nanostructures over macroscopic areas. The dimensions and morphology of nanostructures obtained were characterized by AFM/SEM. The arrays of 65-200nm wide and 125-400nm long gold nano-dots and nano-rods with spacing of 120-220nm were fabricated by IL.

UV-vis absorption spectra of gold nanostructures showed a characteristic peak at ca. 520nm associated with localized surface plasmons. A spectroscopic ellipsometry study of the gold nanostructures was carried out. Raman spectra of a thin film of phthalocyanine adsorbed on gold nanostructures showed an enhancement of Raman scattering of up to 200 times compared with the same film deposited on continuous gold layer.

Post-lithographic processing by annealing was found to improve the optical properties of the nanostructure arrays still further. Annealed samples appear higher and smaller compared to as-prepared samples. AFM images show that all the samples annealed at between 450-470°C for 50-120min retain a regular pattern. XRD analysis of annealed gold nanostructures evinces formation of crystal clusters on the surface.

In order to demonstrate the biosensing capabilities of annealed and as-prepared nanostructures, the LSPR response of nanostructures to changes in the bulk refractive index (RI) was investigated. The RI sensitivity of the annealed samples is found to be 145nm/RIU. Compared to the RI sensitivity value of the as-prepared sample (52.5nm/RIU) this value is ~2.7 times higher due to smaller size of nanostructures and larger spacing between them.

A model biosensing of streptavidin-biotin binding and BSA were successfully performed on as-prepared and annealed gold nanostructures. Measurements were based on the LSPR shift induced by local RI change when proteins are immobilized on the nanostructures. Streptavidin concentrations were washed over the nanostructured surface in cumulative succession ranging from 0.1µg/ml to 0.1mg/ml, followed by an identical protocol with biotin. Characteristic increases and saturation are noted through shifts in the absorption of the LSPR peak at ca. 635nm. Annealed nanostructures demonstrated a higher detection limit (DL) compare to as-prepared one: the DL for BSA is 1.5fM and 50pM for annealed and as-prepared nanostructures, respectively. Our results demonstrate the potential of interference lithography for the application of plasmon-based biosensing devices.

2:20pm **NS+SP-MoA2 Fast Turnaround 3D Nanolithography using Heated Probes – from Nanofabrication to Directed Assembly**, *A.W. Knoll*, *P. Paul*, IBM Research - Zurich, Switzerland, *F. Holzner*, IBM Research - Zurich, ETH Zurich, Switzerland, *J.L. Hedrick*, IBM Research - Almaden, *M. Despont*, IBM Research - Zurich, Switzerland, *C. Kuemin*, IBM Research - Zurich, ETH Zurich, Switzerland, *H. Wolf*, IBM Research - Zurich, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland, *U. Duerig*, IBM Research - Zurich, Switzerland

INVITED

A novel thermal scanning probe lithography (tSPL) method based on the local removal of organic resist materials has been developed at the IBM Research Laboratory in Zurich [1-3]. A polymeric polyphthalaldehyde resist [2-4] responds to the presence of a hot tip by local material decomposition and desorption. Thereby arbitrarily shaped patterns can be written in the organic films in the form of a topographic relief, constrained only by the shape of the tip. The combination of the fast 'direct development' patterning of a polymer resist and the in-situ metrology capability of the AFM setup allows to reduce the typical turnaround time for nanolithography to minutes.

Patterning rates of 500 kHz have been achieved. For this, the mechanics and drive waveform of the scan stage were optimized, achieving high speed linear scanning with an overall position accuracy of ± 10 nm over scan-ranges and scan-speeds of up to 50 µm and 20 mm/s, respectively. A pre-

tension-and-release strategy was used to actuate the cantilever above its resonance frequency of 150 kHz.

Fabrication of three dimensional patterns is done in a single patterning step by controlling the amount of material removal at each pixel position. The individual depths of the pixels are controlled by the force acting on the cantilever.

The structuring capability in the third dimension adds an entirely new feature to the lithography landscape and finds applications e. g. in multi-level data storage, nano/micro-optic components and directed positioning of nanoparticles. For the latter, shape-matching guiding structures for the assembly of nanorods of size 80nm × 25nm have been written by thermal scanning probe lithography [4]. The nanorods were assembled into the guiding structures by means of capillary interactions. Following particle assembly, the polymer was removed cleanly by thermal decomposition and the nanorods are transferred to the underlying substrate without change of lateral position. As a result we demonstrate both the placement and orientation of nanorods with an overall positioning accuracy of ≈ 10 nm onto an unstructured target substrate.

[1] D. Pires, J. L. Hedrick, A. De Silva, J. Frommer, B. Gotsmann, H. Wolf, M. Despont, U. Duerig, and A. W. Knoll, *Science* **328**, 732 (2010).

[2] A. W. Knoll, D. Pires, O. Coulembier, P. Dubois, J. L. Hedrick, J. Frommer, U. Duerig, *Adv. Mat.* **22**, 3361 (2010).

[3] P. C. Paul, A.W. Knoll, F. Holzner, M. Despont and U. Duerig, *Nanotechnology* **22**, 275306 (2011).

[4] F. Holzner, C. Kuemin, P. Paul, J. L. Hedrick, H. Wolf, N. D. Spencer, U. Duerig, and A. W. Knoll, *NanoLetters*, **11**, 3957 (2011).

3:00pm **NS+SP-MoA4 Laser Assisted Electron Beam Induced Deposition of Platinum**, *N.A. Roberts*, University of Tennessee Knoxville, *J.D. Fowlkes*, Oak Ridge National Laboratory, *G.A. Magel*, *T.M. Moore*, Omniprobe, Inc. an Oxford Instruments Company, *P.D. Rack*, University of Tennessee Knoxville

We introduce a laser assisted electron beam induced deposition (LAEBID) process which is a nanoscale direct write method that implements a synchronized electron beam induced deposition (EBID) process with a pulsed laser step for thermal desorption of the reaction by-product. The pseudo-localized (~ 100 nm spot), pulsed laser enables thermal desorption of the reaction by-product without the issues associated with bulk substrate heating, which shortens the precursor residence time and distort pattern fidelity due to thermal drift. Current results show a significant purification of platinum deposits (~35% Pt) with the addition of synchronized laser pulses as well as a significant reduction in deposit resistivity. Measured resistivity from platinum LAEBID structures (1.2×10^4 mW-cm) are more than 3 orders of magnitude lower than standard EBID platinum structures (2.2×10^7 mW-cm) from the same precursor and are lower than the lowest reported EBID platinum resistivity with post-deposition annealing (1.4×10^4 mW-cm).

3:40pm **NS+SP-MoA6 Parallel Stacking of Extended π -conjugated Molecules on Si(100)-H Surface**, *M.Z. Hossain*, Gunma University, Japan, *H. Kato*, Osaka University, Japan, *M. Kawai*, The University of Tokyo and RIKEN, Japan

Understanding and controlling of intermolecular interaction in highly organized π -conjugated molecules is crucial for the development of the high performance organic devices. Molecule-molecule interaction through frontier orbital states is assumed to be substantially varies with the packing pattern and intermolecular distance. H-terminated Si(100) surface has appeared as an ideal template for controlled stacking of π -conjugated molecules, where the intermolecular distance is defined by the dimer-dimer distance on the surface. To date, a number of studies have been reported on the controlled growth of different types of molecular assemblies and their junctions on the surface. It is expected that intermolecular interaction between such assemblies should strongly varies with substituent and extent of π -conjugation of the molecules. Here we report various nanopattern formation with some simple acene molecules such as 9-vinyl anthracene, 2-vinyl naphthalene and styrene on H-terminated Si(100) using scanning tunneling microscope (STM) and ultraviolet photoelectron spectroscopy (UPS).

Controlled stacking of styrene molecules on H-terminated Si(100) surface through chain reaction mechanism is well known. Self-directed growth of molecular stacking is exclusively directed along the dimer row on the surface, where the phenyl rings are stacked in parallel along the dimer row. Unlike styrene molecule, 9-vinyl anthracene forms both orderly stacking pattern along the dimer row and disorderly nanopattern on the surface. The relative appearances of these orderly and disorderly nanopatterns in STM

images depend on the applied sample bias while scanning. At lower bias, the orderly pattern appears much brighter than that of the disorderly pattern. This contrast difference between two structures relates to the enhanced π - π interaction in the case of orderly stacked nanopattern. We also observe that the orderly nanopattern of anthracene molecules undergoes reversed chain reaction very frequently compared to that of styrene molecule.

The 2-vinyl naphthalene molecules form relatively shorter assemblies along the dimer row. Some short disorderly structures are also seen in STM images. UPS measurements of different surfaces containing high-density nanopatterns of these acene molecules have been performed. The observed peaks in UPS spectra are reasonably in agreement with the theoretical calculations reported earlier. The details of the UPS spectra and the reaction mechanism of each molecule forming different nanopatterns will be discussed.

4:00pm NS+SP-MoA7 Kinetics of disilane reaction on Si(100)-(2x1): Flux, Temperature, and H-coverage Dependence, D. Dick, J.-F. Veyan, University of Texas at Dallas, P. Mathieu, McGill University, Canada, J.N. Randall, Zyvex Laboratories, Y.J. Chabal, University of Texas at Dallas

Atomic Layer Epitaxy (ALE) is a fundamental process in the Atomically Precise Manufacturing (APM) of nanoscale devices. Si₂H₆ has been shown to be a good precursor molecule for patterned growth on Si(100) using Chemical Vapor Deposition (CVD). For ALE of silicon, three parameters have to be considered: the incident Si₂H₆ flux, the temperature, and partial H coverage of the surface. These parameters have been investigated experimentally using in-situ infrared absorption spectroscopy to characterize the nature and coverage of species on a Si(100)-(2x1) surface in a well-controlled environment (2x10⁻¹⁰ Torr base pressure).

The flux dependence was studied over two orders of magnitude and temperature dependence from 173 K to 473 K for varying fluxes. It was found that the nature of SiH_x species formed at the surface was strongly dependent on the flux, with higher silanes (e.g. x>1) for higher fluxes. Furthermore, the time required for saturation also decreased with increasing flux and temperature.

The impact of partial H coverage was also investigated with H coverage from 0.01 to 1 ML Monolayer, achieved by partial desorption of a H saturated surface. On the substrate's surface has been also investigated with FT-IR under UHV conditions. It has been found that even a very small amount of Hydrogen (~1% ML) substantially reduces the chemisorption of disilane on the clean parts of Si(100)-(2x1).

This complex dependence on flux and temperature arises from the complex and highly temperature dependent adsorption/dissociation behavior of disilane on Si(100). The dependence on partial H coverage highlights the spatial requirements of the dissociation products, as uncovered in our earlier work.¹

1 J.-F. Veyan, et al., Journal of Physical Chemistry C 115, 24534.

4:20pm NS+SP-MoA8 SPM Lithography on Silicon Reconstructed and Hydrogen-Passivated Surface, J. Fu, K. Li, N. Pradeep, L. Chen, R. Silver, National Institute of Standards and Technology

We are using Scanning Probe Microscope (SPM) to write patterns directly on a single crystal silicon surface that was reconstructed and hydrogen-passivated in the ultra high vacuum (UHV) chambers, and are followed by the process of reactive ion etching to transfer the patterns into the silicon bulk. The patterns were written either by an atomic force microscope (AFM) in the ambient or by a scanning tunneling microscope (STM) in UHV chambers and was immediately proceeded by an oxidation process in a separate vacuum chamber. AFM or STM patterned samples were immediately transferred to a RIE chamber via an argon back-filled inflatable glove box.

In terms of patterning, the AFM in the ambient environment and the STM in the UHV both can perform lithograph; however, the mechanism are quite different: the AFM is adding species, OH⁻, to the surface, and the STM is removing species, H, from the silicon surface.

The features patterning by the AFM prior to RIE process were 1~2nm in height, and were 15~20nm height after RIE and 6nm wide (FWHM) that were measured and confirmed by a critical dimension AFM (CD-AFM). For the features patterning by STM, it was conjectured the height were 0.2~0.3nm prior to RIE. After the RIE process, the height was measured to be 0.7nm.

4:40pm NS+SP-MoA9 Ultra-High Frequency Surface Acoustic Wave Generation in Silicon Using Inverted Nanoimprint Lithography, S. Büyükköse, University of Twente, Netherlands, B. Vratzov, NT&D – Nanotechnology and Devices, Germany, D. Ataç, J. van der Veen, University of Twente, Netherlands, P.V. Santos, Paul-Drude-Institut für Festkörperelektronik, Germany, W.G. van der Wiel, University of Twente, Netherlands

Surface acoustic waves (SAWs) are widely used and very important phenomena in both research and industry. SAWs are mechanical vibrations propagating along the surface by confining the acoustic energy over a depth of typically one wavelength. In piezoelectric materials, they can be excited through the inverse piezoelectric effect by using interdigital transducers (IDTs): two interlocking comb-shaped metallic electrode pairs. A piezoelectric potential wave accompanies the mechanical wave. The unique SAW properties make them suitable for wide range of applications. Among the most exciting applications of SAWs are acousto-optical modulators as well as the control of excitons, electrons, and spins in semiconductors. For almost all SAW applications, there is a strong demand for higher frequencies, for example to enhance processing speed or to reach the quantum regime. There are two main factors determining the IDT resonant frequencies: the acoustic properties of the substrate, and the IDT period constrained by lithography resolution. In latter case, the resolution of standard photolithography (minimum finger width of approx. 0.5 μ m) limits the operation frequency to around a few GHz, even for high acoustic-velocity substrates.

In this study, an alternative lithography technique, "step-and-flash nanoimprint lithography" (SFIL), with a novel material system for lift-off was used to reach very high resolution and higher reproducibility. Hydrogen silsequoxane (HSQ) was used as a planarization layer and an excellent etching mask to get inverted replication of the IDT features on the SFIL template. A sufficient undercut profile of the electrode features, which is essential for metal lift-off at nanoscale, was successfully achieved. Very high critical dimension (CD) control has been obtained for the electrode dimensions from 125nm down to 65 nm. While this method has the advantage of EBL resolution, it is nearly substrate independent with higher throughput compared to EBL. For the IDT fabrication, we have deliberately chosen a rather standard Si substrate to demonstrate that our method can result in extremely high-frequency SAW devices, which can be monolithically integrated with common electronic circuitry. Integration of high-frequency SAW devices is normally restricted by the incompatibility of piezoelectric films with CMOS processing. We showed that SAW delay line devices with 125nm down to 65 nm metal lines can reach resonance frequencies up to 16 GHz in ZnO/SiO₂/Si multilayer system, which is the highest frequency for ZnO based transducers on Si reported so far. The finite element analysis confirmed the results and showed good agreement with the experiment.

5:00pm NS+SP-MoA10 Variance of Proximity Effect Correction Parameter Measured on Silicon, D.A. Czapski, L.E. Ocola, Argonne National Laboratory

We present data showing that the relative intensity of the backscattered electrons, h , to primary write electrons varies depending on the experimental setup. Our data is consistent with the wide range in values reported in the literature for h . The value of h was determined using a doughnut and cross method [1] where the range of the backscattered electrons was measured to an uncertainty of less than 1%. We find that using this method to determine h provides values that are dependent on the dose of the doughnut. Such a result raises questions on the effectiveness of standard proximity effect correction models (PEC) if they rely on a single h value. Standard PEC models attempt to load level the dose received by the desired pattern in the e-beam resist from all sources of electrons, including the forward and backward scattered electrons during an electron beam exposure.

The relative dose of the backscattered electrons was measured using a set of intersecting lines at the center of tori patterns in a doughnut and cross method [1], (Fig. 1). The backscattered electron dose contribution was varied by changing the dose of the tori with respect to the dose of the intersecting lines as can be seen in Fig. 2. The expected behavior would be a consistent ratio of the backscattered contribution and the line dose; however, as the backscattered electron dose is decreased, the relative contribution to the pattern increases faster than the line dose contribution (Fig. 3). The causes of this phenomenon are not certain yet, but the implications could change existing PEC models. Through further study of this phenomenon, it is possible that the models used in PEC could be updated to accommodate this data and therefore give more accurate dose assignments.

[1] D. A. Czapski, L. E. Ocola, Appl. Phys. Lett. 99 192105 (2011).

5:20pm NS+SP-MoA11 Nanopatterning of Poly(N-isopropylacrylamide) based Hydrogel – Gold Nanoparticle Composite, K.J. Suthar, D.C. Mancini, R.S. Divan, Argonne National Laboratory, O.N. Ahanotu, University of Michigan

This paper presents the nanopatterning of the hydrogel-gold nanocomposite. We synthesized water based colloidal suspension of covalently bound gold nanoparticles (5-10nm) on the backbone of Poly(Allyl amine) by reduction of gold salt on the amine groups of polymeric chain. Poly(N-isopropylacrylamide) was dissolved in Poly(Allyl amine) based gold colloidal solution. This solution then spun-coated on Hexamethyldisilazane primed Si wafer for nanolithography. The hydrogel precursor was dried in air. Resulting thickness of the hydrogel precursor was approximately 1 μm . The samples were then exposed to 110-180 $\mu\text{C}/\text{cm}^2$ e-beam. The exposure dose was optimized for different thickness of precursor. Different characterization techniques such as UV-vis spectroscopy, differential scanning calorimetry, FTIR, scanning electron microscopy, and atomic force microscopy were employed for characterization. Thus, gold nanoparticles were incorporated into a three dimensional, cross-linked, polymeric hydrogel network by nanopatterning technique. With the ability of hydrogels to expand or contract with changes in pH and temperature, the spacing between nanoparticles can be controlled, allowing a single material being able to resonate at different frequencies. The ability to perform lithography to form a patterned hydrogel with homogeneous nanoparticles opens the door to development of nanoswitches, sensors, MEMS as well as drug delivery devices.

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