

Tuesday Evening Poster Sessions, November 4, 2003

Nanometer Structures

Room Hall A-C - Session NS-TuP

Poster Session

NS-TuP1 Electrical Characteristics of Semiconductor-Atomic Superlattice for Silicon-on-Insulator Application, Y.-J. Seo, DAEBUL University, Korea; R. Tsu, University of North Carolina at Charlotte

Silicon on insulator (SOI) structure is a critical material for future ultra-large scale integration (ULSI). Recently, we had been reported that the Si-O superlattice can serve as an epitaxially grown insulating layer as possible replacement of SOI. Up to a bias of 30 V, the field inside the multi-layer structure reaches $\sim 3 \times 10^7$ V/cm. There is no sign of breakdown. However, the low voltage isolation is not quite sufficient for implement as a substitute for silicon on insulator. In this paper, the monolayers of oxygen atoms sandwiched between the adjacent silicon layers formed by ultra high vacuum-chemical vapor deposition (UHV-CVD). This multi-layer Si-O superlattice forms a new type of superlattice, semiconductor-atomic superlattice (SAS). According to the preliminary results, high-resolution cross-sectional transmission electron microscopy (HRTEM) shows epitaxial system. Also, the current-voltage (I-V) measurement results show the stable and good insulating behavior with high breakdown voltage. It is apparent that the system may form an epitaxially grown insulating layer as possible replacement of SOI, a scheme investigated as future generation of high efficient and high density CMOS on SOI. Since our scheme is epitaxial, three-dimensional integrated circuits (3D-ICs) may finally be realized in silicon-based technology. Therefore it is important to determine how good is the epitaxially grown silicon beyond a relatively thick Si-O superlattice. This work was supported by Grant(R05-2002-000-00565-0) from the Basic Research Program of the Korea Science & Engineering Foundation.

NS-TuP3 Synthesis of Nanocrystalline Semiconductors and Phosphors by Thermal Self Assembly, M. Abboudi, Universite Abdelmalek Essaadi, Morocco; S.Y. Seo, J. Bang, University of Florida; A. Benali, Universite Abdelmalek Essaadi, Morocco; P.H. Holloway, University of Florida

A new method has been used to produce luminescent and semiconducting nanopowders by thermo-decomposition of precursors prepared in situ by a direct solid state reaction. This represents a new self assembly approach for the synthesis of nanocrystalline materials. Oxide phosphors prepared by this method include ZnGa₂O₄ doped with europium or manganese, and Y₂O₃ doped with europium. All the synthesized powders have been characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The photoluminescence and the cathodoluminescence from these phosphors with an average particle size of ~ 50 nm have been studied with varying doping concentrations. Optimized concentrations will be reported and the luminescent spectra shown to be characteristics of the normal transitions for the dopants. The relative luminescence efficiencies will be shown to be good for these nanoparticles. We have also prepared nanocrystalline GaN powders, and will report on the defect structure from luminescence data. Finally, synthesis of Fe₂O₃ with particle diameters ≤ 25 nm, and Ce_{0.8}Gd_{0.2}O₃ with a specific surface area of 29 m²/g will be reported. Potential applications of these nanoparticles to phosphors, catalysts, photovoltaics, data storage, fuel cells and sensors will be discussed.

NS-TuP4 The Effects of Molybdenum-Oxide and Diamond on Field Emission, T. Tyler, D. Jaeger, A. Kvit, North Carolina State University; V. Zhirnov, Semiconductor Research Corporation; J. Hren, North Carolina State University

Refractory metals such as molybdenum and tungsten are frequently used in field emission applications, most often in the form of single tips or arrays of tips. Such field emitters have been studied in great detail over the past thirty years. The addition of an 'intentional' coating material (e.g. dielectric deposits such as aluminum-oxide or diamond) to improve emitter performance has been widely studied as well. However, there has been a lack of control of substrate effects (e.g. the presence and nature of oxides) in combination with coating effects. Carefully controlled morphological and compositional information is now required for a more complete analysis. We report here on combined studies of field emission, with high-resolution transmission electron microscopy (HRTEM), with computer simulations of local electric fields. Current versus voltage data is obtained during field emission, while HRTEM is used to determine morphology and composition (using electron energy loss spectroscopy). Computer simulations of

electrostatic effects, employing finite element methods, are then conducted using the morphologic and compositional information of the composite emitter structure, obtained from HRTEM. The magnitude and distribution of the surface potential barrier and the local field strength at the apex of the field emitter can thus be determined. The results also can provide information on the materials' electronic properties, such as the dielectric constant, trap density, and carrier velocity. The non-destructive nature of these experiments makes comparison studies possible; e.g. molybdenum needles, both oxidized and non-oxidized, are compared with needles coated with layers of nano-diamond.

NS-TuP5 Formation of Nanoporous Noble Metal Films by Electrochemical Dealloying of Pt_xSi_{1-x}, J.C. Thorp, K. Sieradzki, N. Dimitrov, S.T. Picraux, Arizona State University

Electrochemical dealloying of metallic alloy mixtures provides a novel way to form nanoporous structures. In the present study we demonstrate the extension of this concept to metal-silicon alloys on silicon platforms for Pt_xSi_{1-x}. The Pt_xSi_{1-x} (x = 50 and 25%) alloys are formed by deposition and thermal treatment. Thermal reaction of Pt films is used to form PtSi silicide layers and co-deposition for more silicon rich alloys. The films (200 to 800 nm thick) are then dealloyed in concentrated HF by an electrochemical process that leaches out the silicon. Anodic polarization curves are used to establish the optimum potential for dealloying, for example near +400 mV (SCE) for PtSi with current densities of approximately 10 mA/cm². Rutherford Backscattering Spectrometry (RBS) demonstrates the formation of a pure Pt layer on the metal silicide layer as dealloying process progresses and thus provides a direct observation of the dealloying kinetics. The resulting morphology of the nanoporous noble metal structures is determined by scanning electron microscopy. Results are presented for various Pt silicon alloys and dealloying conditions, and preliminary results will be discussed for Au silicon alloys. These nanoporous noble metal thin film structures provide high surface area electrodes on Si. Such nanostructures are of interest for microscale electrochemical sensing and microfuel cells.

NS-TuP8 Solvothermal Synthesis of Nanocrystalline γ -Fe₂O₃ in Toluene, C.-S. Kim, J.-H. Park, B.K. Moon, H.J. Seo, Pukyong National University, Korea; B.-C. Choi, Pukyong National University, Korea, South Korea

The synthesis of γ -Fe₂O₃ nanoparticles has been performed in solvothermal route. The nanocrystalline particles were obtained after synthesis using two different temperatures of 130°C and 180°C for 10 hrs in an autoclave, where iron pentacarbonyl is thermally decomposed in toluene solutions in the presence of trimethylamine N-oxide as an oxidant. X-ray diffraction and transmission electron microscopy shows that the product has uniform maghemite structure with average particle size below 30 nm. The specific surface area of the γ -Fe₂O₃ nanocrystalline powder was investigated using BET surface area analyzer. Influence of synthesis conditions such as synthesis temperature and molar ratio of precursor to solution on the size and size distribution of the product was also discussed.

NS-TuP9 Nanopipes in Single Crystal Transition-metal Nitride Layers, D. Gall, Rensselaer Polytechnic Institute

Nanopipes are 1-nm-wide open pores that extend through the entire thickness of epitaxial NaCl-structure transition-metal nitride layers. They form due to a combination of anisotropic surface diffusion and atomic shadowing effects. Their shape, orientation, and arrangement can be controlled by ion-irradiation and deposition angles. CrN, TaN, ScN, and TiN layers were grown on MgO(001) at 600-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N₂ and N₂+Ar discharges at 3-20 mTorr. These deposition conditions result in a highly anisotropic surface diffusion with hop-rates that are 7 orders of magnitude smaller on (111) versus (001) surfaces. This anisotropy leads, during growth under limited adatom mobility conditions, to kinetic surface roughening and the development of deep surface cusps which cause atomic shadowing and the formation of nanopipes that are elongated along the [001] growth direction. The nanopipes have rectangular cross-sections and form self-organized arrays aligned in orthogonal [100] and [010] directions, precisely replicating the in-plane correlation of the surface morphology. Non-normal deposition increases the level of atomic shadowing and introduces a controlled tilt to the nanopipes. Increasing the N₂+Ar ion irradiation flux or decreasing the N₂ partial pressure (and, hence, the steady-state N coverage) during growth provides a corresponding increase in cation

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surface mobilities leading to smoother surfaces, less atomic shadowing, and partial or full suppression of nanopipe formation.

NS-TuP10 Nanopatterning of Hydrogen Silsesquioxane Resist, M.J. Word, I. Adesida, University of Illinois at Urbana-Champaign

Creating nano-scaled structures in semiconductor materials generally begins with the use of high-resolution lithography techniques and resists. Electron beam lithography is capable of creating isolated structures less than 10 nm in width when utilized with high-resolution resists such as hydrogen silsesquioxane (HSQ). In addition to these isolated structures, it is also important to characterize the resist when more complex and denser structures are required. In our study we characterized the resolution of HSQ resist in the form of densely packed gratings. We began by examining the surface of very thin films of HSQ resist down to a thicknesses of 100 Å in order to determine the limits for successful processing using lithography techniques. Using a JEOL JBX-6000FS electron beam lithography machine operating at 50 kV with a current of 20 pA, we then exposed samples of HSQ at various film thicknesses with gratings having periods as small as 20 nm. We use the results to characterize the resolution limits of HSQ with respect to film thickness, dosing, and grating periodicity. In addition, we discuss the transfer of nanometer-scale patterns into InP and other semiconductor materials with exposed HSQ gratings acting as the etch mask. H. Namatsu, *J. Vac. Sci. Technol. B* 19, 2709 (2001).

NS-TuP11 On the Study of Growth Behavior of Carbonaceous Tips by Electron Beam Induced Deposition using Preprocessing Methods, S.H. Kim, Korea Electronics Technology Institute, South Korea; *Y.J. Choi,* Korea Electronics Technology Institute, South Korea

For the investigation of high aspect ratio structures with SPM, the cantilevers with very sharp and long tips are useful. The carbon nanotube(CNT) tips and electron beam deposited(EBD) tips are effective candidates for the high aspect ratio tips. Although EBD tips are duller than CNT tips, they have an advantage of simple fabrication process over the CNT tips. EBD tips can be simply fabricated by aligning the electron beam directly down the vertical axis of Si cantilever and then irradiating a single spot on the cantilever for a proper time in the dominant atmosphere of residual gases generated by the oil of the diffusion pump of the Scanning Electron Microscope(SEM). The height and the base diameter of the EBD tips can be controlled by adjusting the control parameters of the SEM. However, the EBD tips cannot grow over 1µm in the residual gas atmosphere. We could enhance the height of tips by dipping the catilever into the organic solvents which contain aromatic or aliphatic hydrocarbon, drying it in the vaccum chamber and irradiating electron beam. With this process, we could acquire the tip whose base diameter is 0.180µm and effective length is 3.18µm. In addition, we observed that the growth behavior of the tips are different in accordance with the species of the chemicals and we will discuss the effects of the organic solvents on the growth of the tips. Albert Floch, Jordi Servat, *J. Vac. Sci. Technol. B*, Vol 14, No. 4 Jul/Aug (1996). M.Wendel, H.Lorenz, and J.P.Kotthaus, *Appl. Phys. Lett.* 67(25) (1995).

NS-TuP12 Probing Adhesion and Friction on Nanostructured Surfaces with Chemical Force Microscopy, C.L. Berrie, J.E. Headrick, University of Kansas

Chemical functionalization of AFM probe tips allows regions of different composition on the surface to be identified even in the absence of topographic variations. Unfortunately, many of the established chemical-functionalization methods lead to a significant increase in the size and curvature of the tip radius, which effectively sacrifices the resolving ability of the AFM measurement. In this work, we have chemically-modified commercially-microfabricated Si₃N₄ AFM tips with a variety of self-assembled alkylsilane monolayers having distinct terminal functionalities, such as -CH₃, -CH₂Br and -COOH, using a fabrication process that minimizes undesirable resolution-loss due to tip growth. We have measured the adhesion forces and friction loops between these functionalized tips and various substrates, including nanostructured substrates where the chemical composition of the surface varies on the nanometer length scale (for example from hydrophobic to hydrophilic). The nanostructured surfaces are created using the AFM. These results will help us to understand the resolution limits of these techniques by allowing the investigation of the sensitivity of the technique to pattern size.

NS-TuP14 In-situ Tip Preparation and Nanoscale Surface Modification using STM Manipulation, V. Iancu, A. Deshpande, S.-W. Hla, Ohio University

Single atom manipulation with a scanning tunneling microscope (STM) tip on crystal surfaces requires an extremely fine control over the tip-atom-surface junction. The shape of the STM-tip and the chemical elements that constitute the tip-apex are vital for a successful atom manipulation with atomic scale precisions. Here we report an in-situ tip preparation technique useful to fabricate stable STM-tips with a known chemical element at the tip-apex. The experiments are conducted at an ultra-high-vacuum conditions on a Ag(111) surface at 4.8 and 75 K sample temperatures. During the experiment, the STM-tip, made of polycrystalline tungsten wire, is gently dipped into the substrate and the tunneling voltage is increased to 3 V. The penetration depth is precisely controlled. The shape of the holes created by the tip dipping indicates that the tip becomes sharper by repeating the procedure. This is due to the local heating during the tip-sample mechanical contact that re-shapes the structure of the tip-apex. In addition, variation of the tip-height and tunneling voltage during the procedure results in different impact force. By applying suitable impact force with the STM-tip, atomic scale surface steps and Ag islands can be created locally. This entire procedure will be useful to conduct new nanoscale experiments or to test the strength of the material at an atomic level. S.-W. Hla, K.-F. Braun, K.-H. Rieder, "single atom manipulation mechanisms during a quantum corral construction", *Phys. Rev. B* rapid communication (2003) in press. L. Bartels, G. Meyer, K.-H. Rieder, "Inducing all steps of a chemical reaction with the scanning tunneling microscope tip: Towards single molecule engineering", *Phys. Rev. Lett.* 85 (2000) 2777-2780.

NS-TuP15 Tomographic Reconstruction of Doping Profile and Device Structure in Si MOSFET Devices with a sub 10 nm Spatial Resolution, R.K. Bansal, J.M. Fitz-Gerald, R. Hull, D.H. Anjum, University of Virginia

Due to a phenomenal reduction in the size of semiconductor devices over the last two decades there is a need to develop better characterization methods which can probe the devices in three dimensions with a high spatial resolution. The present work aims at tomographic reconstruction of the device structure and doping profile in semiconductor devices with sub-10 nm resolution. This involves using a Focused Ion Beam (FIB) to sputter away layers of atoms and subsequently image the cross-section of the device using a high resolution scanning electron microscope (SEM). This process is repeated, followed by concatenation of these images in the computer, to obtain a three dimensional reconstruction of the device. The SEM used for this work is the state-of-the-art JEOL 6700F field emission SEM which has a spatial resolution of 1nm. Also under investigation is the possibility of observing the spatial dopant distribution in the device and the enhancement of the doping contrast by using hydrogen surface passivation. This study is currently being done on short channel length (50nm -1µm) MOSFETs with strained and unstrained Si channel and can be extended to other devices and material systems.

NS-TuP16 Imaging of DNA Strands with the Low Energy Electron Point Source (LEEPS) Microscope, A. Eisele, Universität Marburg, Germany; *B. Völkel, M. Grunze,* Universität Heidelberg, Germany; *A. Götzhäuser,* Universität Marburg, Germany

A low energy electron point source (LEEPS) microscope is used to image freestanding DNA multistrands. These span 100 nm wide openings in a thin silicon sample holder. The holographic images are analyzed by assuming a mask model and vacuum wave propagation. We extract the correct source-to-object distance by the analysis of cuts through numerical reconstructions in the object region with an accuracy of 40 nm. Upon variation of the lateral and axial source position, the reconstructions show reproducible object structures and focus behavior. The smallest reproducibly resolved features have dimensions of 1 nm. Due to the low energy (40 eV) of the field emitted electrons, LEPS microscopes generate images with a much higher contrast than conventional electron microscopes.

NS-TuP18 Second Harmonic Piezoresponse Force Microscopy: A Probe of High Order Ferroelectric Processes, R. Shao, University of Pennsylvania; *S.V. Kalinin,* Oak Ridge National Laboratory; *D.A. Bonnell,* University of Pennsylvania

Piezoresponse Force Microscopy (PFM) has been widely accepted as an important technique for imaging ferroelectric domains. The principle of PFM is the detection of the electromechanical response to an ac voltage applied at a tip/surface contact. There are two unresolved issues associated with PFM. The first is the degree of perturbation to ferroelectric

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domain polarization imposed by the ac voltage. The second is a dilemma involving switching mechanisms during acquisition of the hysteresis loop. To address these issues, we have measured the second harmonic of the electromechanical response to the ac imaging voltage on various ferroelectric materials as a function of both frequency and amplitude of the voltage. A theoretical model has been established that relates the ferroelectric relaxation to the second harmonic response. The approach is extended to an imaging technique, Second Harmonic Piezoresponse Microscopy, that maps the distribution of relaxation times on surfaces by acquiring the spatial distribution of the second harmonic response.

NS-TuP19 Lithographic Patterning using Near-field Scanning Optical Microscopy, R.E. Hollingsworth, ITN Energy Systems, Inc; C. Veauvy, M. Treaster, J.D. Beach, R.T. Collins, Colorado School of Mines

We report the development of a near-field scanning optical microscope (NSOM) designed specifically for direct write lithography on 4" substrates. Direct write lithography is ideally suited to research use where rapid turn around, flexible pattern generation and much lower cost than production tools are very important. At present, electron beam lithography is the most commonly used direct write technique, although scanning probe microscopes are receiving increasing attention. The advantages of NSOM lithography over these other direct write approaches are the ability to use conventional optical photoresists and to combine near-field with far-field optical exposure. As an optical technique, NSOM also avoids concerns of high-energy electron damage and vacuum compatibility inherent to e-beam lithography. Our approach uses state of the art mechanical translation stages that take steps a fraction of the typical NSOM resolution. This allows patterning over typical wafer dimensions with none of the stitching errors inherent in other techniques. The microscope also functions in standard NSOM characterization modes allowing, for example, nanoscale topography and reflectance to be measured and used in feature characterization and pattern registration. In this presentation, we will discuss the microscope design, performance tests, and photoresist process development for 100nm scale features and for pattern transfer into substrates and films. Microscope use in example applications such as quantum point contacts, surface plasmon enhanced near-field optics, and nucleation sites for seeded film growth will be presented.

NS-TuP20 Electroless Metal Discharge Layers for Electron Beam Lithography, S.L. Brandow, M.-S. Chen, W.J. Dressick, R. Bass, Naval Research Laboratory; E. Dobisz, Hitachi Global Storage Technologies

Substrate charging during e-beam lithography on non-conductive materials can lead to severe problems in pattern placement accuracy and critical dimension (CD) error. Current methods of controlling charge include the use of conducting polymers or evaporated metal films as charge dissipation layers. We report an alternative approach utilizing ultrathin (i.e., 15-30 nm) Cu films deposited by electroless metal deposition. Our method involves the sequential chemisorption of an aminosiloxane film to the substrate of interest, binding of a colloidal Pd/Sn electroless catalyst, and brief immersion in an electroless Cu bath to deposit the ultrathin Cu film. This ligand based approach permits sufficient control of Cu thickness and uniformity to satisfy electrical conductivity, adhesion, and transparency constraints required for discharge layers. The deposition process is performed under ambient, aqueous conditions which are track-line compatible and thus should have cost advantages over conventional CVD based metallization processes. The grounded Cu film, deployed here as a resist underlayer, eliminates the 0.1 - 0.4 micron subfield stitching errors normally observed in the absence of the Cu film during resist patterning on a glass or insulating substrate. The Cu is readily removed using a nitric acid wet etch following patterning.

NS-TuP21 Metal Pattern Transfer from Microstructured Self-Assembled Monolayer Templates to Polymer Substrates by an Imprinting Method, S. Imura, N. Saito, H. Sugimura, O. Takai, Nagoya University, Japan

Nanoimprint lithography is expected to play a crucial role in device nanoprocessing. The method has been employed in order to transfer a minute structure on a mold to a polymer film. Besides fabrication of such 3D polymer nanostructures, nanopatterning a functional material other than polymers through nanoimprint is of further interest. Here we show the first demonstration of metal pattern formation by a imprinting method in which a metal micropattern deposited on a microstructured template was directly transferred onto a polymer substrate. First, a microtemplate was fabricated as follows. An organic self-assembled monolayer was formed from 1-undecanol on a Si substrate of which surface oxide was removed by HF etching. This monolayer was micropatterned by a photolithographic method. Due to irradiation at a

wavelength of 172 nm, the monolayer was photochemically decomposed and the underlying Si was oxidized. Consequently, a micropattern on a photomask was printed on the sample as a micropattern consisting of the unirradiated monolayer and photochemically formed SiO₂. Next, this microtemplate was immersed in a tin solution, a palladium solution and a Ni electroless plating solution, in that order. Ni was deposited selectively on the unirradiated monolayer while the oxide surface remained undeposited. Finally, this Ni micropattern deposited on the template was transferred onto a polymer substrate. The template was heated to a temperature of 180 °C and pressed into a polymethylmetacrylate (PMMA) substrate at a pressure of 10 MPa. The Ni micropattern was successfully transferred from the template to the PMMA substrate. @FootnoteText@ @footnote 1@H. Sugimura et al. Langmuir 16, 885 (2000).

NS-TuP22 Photolithographic Structures with Precise Controllable Nanometer-Scale Spacings Created by Molecular Rulers, M.E. Anderson, L.P. Tan, M. Mihok, H. Tanaka, M.W. Horn, P.S. Weiss, Pennsylvania State University

The combination of conventional lithographic techniques with chemical self-assembly allows for the creation of nanostructures whose spacing and edge resolution reach nanometer-scale precision. The controlled placement and thickness of self-assembled multilayers composed of alternating layers of α -mercaptoalkanoic acids and coordinated metal ions form precise "molecular ruler" resists to produce tailored, lithographically defined patterns. This resist is selectively deposited onto initial parent gold structures, metal is deposited, and the resist is lifted off, thereby leaving daughter structures whose spacing from the parent depends on the thickness of the resist. For future device fabrication with this technique, it would be advantageous to position these gaps selectively on the surface. We report here a method to accomplish this purpose by combining photolithography and molecular rulers. After forming the molecular resist, conventional photoresist is spin-cast onto the wafer and the photomask is aligned with the parent structure to place daughter structures only in selected locations. After exposure, development, metal deposition, and lift-off of both the photoresist and molecular resist, the final product is a wafer with daughter structures and gaps selectively oriented to create the desired hierarchical nanostructures. @FootnoteText@ @footnote 1@ A. Hatzor and P.S. Weiss, Science 291, 1019 (2001). @footnote 2@ M. E. Anderson, R. K. Smith, Z. J. Donhauser, A. Hatzor, P. A. Lewis, L. P. Tan, H. Tanaka, M. W. Horn, and P. S. Weiss, Journal of Vacuum Science and Technology B 20, 2739 (2002).

NS-TuP23 Formation and Characterization of Nanopores, T. Schenkel, V.R. Radmilovitch, A. Persaud, S.-J. Park, Lawrence Berkeley National Laboratory; J. Nilsson, Lawrence Livermore National Laboratory

The ability to form holes in membranes with diameters of only a few nanometers (1 to 10 nm) is of interest in many fields of nanometer scale science including single molecule studies, ion proximity lithography, and single atom doping. We report on studies of nanopore formation by local deposition of material in a dual beam focused ion beam system (FIB). Large holes with diameters of tens of nanometers are closed by the local deposition of platinum and TEOS oxide. We compare results from electron beam and ion beam assisted deposition of materials. Hole structure evolution is monitored in situ during hole closing by SEM. Hole profiles, local crystalline structure and materials composition are characterized ex situ by TEM. Nanopores with diameters in the 5 nm range have been formed in low stress silicon nitride membranes. We will discuss process reproducibility, and mechanisms of local structure evolution. @footnote 1@ @FootnoteText@ @footnote 1@ This work was performed at the National Center for Electron Microscopy at the E. O. Lawrence Berkeley National Laboratory and was supported by the National Security Agency and Advanced Research and Development Activity under Army Research Office contract number MOD707501, and by the U. S. Department of Energy under contract No. DE-AC03-76SF00098.

NS-TuP24 Probe-Scanned Traces with Chemical Reversibility on Organosilane Self-Assembled Monolayer Surfaces, N. Saito, S.L. Lee, H. Sugimura, O. Takai, Nagoya University, Japan

Amino-terminated self-assembled monolayers (SAMs) on silicon substrate have a potential as templates for biosensor or molecular devices. Since amino groups are able to link with target molecules such as deoxyribonucleic acid (DNA) and antibody-forming cell, many researchers had investigated amino-terminated SAMs. To fabricate components of future micro-devices, such templates must offer high chemical reactivity which is restricted to specific micro-regions. Thus, the amino-terminated

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regions must be prepared on given points of a substrate. Such a microstructure can be accomplished by maskless lithography techniques such as focused ion beam lithography and electron beam lithography. However, these lithography techniques cause a great deal of damage to the amino-terminated surface of a SAM due to the excessive energy applied. Considering this, we determined we had to develop a soft chemical lithography process for the reversible oxidation-reduction reaction of amino groups. Scanning probe lithography (SPL) is based on electrochemical theory and can be employed to realize such a soft process by controlling the applied potential. SPL had been applied in many cases, however, for the elimination of SAMs. In our present research, we have attempted, through chemical lithography, to produce amino-terminated regions on a sample surface without changing any other part of molecule. Amino-terminated SAM samples were prepared from p-aminophenyltrimethoxysilane through chemical vapor deposition. The amino-terminated surfaces were converted into nitroso-terminated surfaces at positive bias voltages. Moreover, the nitroso-terminated surfaces were reconverted into amino-terminated surfaces. The changes of functional groups on the surfaces were traced by Kelvin probe force Microscopy and atomic force microscopy.

NS-TuP25 Exploration of Chemical Bonding Forms for Producing Organic Monolayers Directly Attached to Silicon, N. Maeda, N. Saito, H. Sugimura, O. Takai, Nagoya University, Japan

Self-assembled monolayer (SAM) formed through the chemical reaction between 1-alkene and hydrogen-terminated silicon (Si-H) is an attractive material for molecular electronic devices, since such a monolayer is directly attached to Si without inserting an oxide layer. This is advantageous for electronic applications of the SAMs and is distinct from an organosilane SAM on Si which needs the oxide interlayer. Furthermore, such a directly-bonded SAM is chemically durable to HF solution more than the organosilane SAM.¹ However, an understanding of chemical reactivities of Si-H surfaces to organic molecules is still in an insufficient level. Here we report on SAM formation on Si-H from various precursor organic molecules including 1-hexadecan, phenylacetylene, 1-undecanol, 4-bromomethylbiphenyl, p-phenylenediamine, terephthalaldehyde, etc. Si-H samples were prepared through the etching of Si(111) substrates in 5%-HF. A Si-H sample was then refluxed at a temperature ranging from 100 to 180 °C for several hours in a precursor liquid or a organic solution of a precursor under an atmosphere purged with N₂.² The treated sample was examined with a water contact angle measurement, X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy in order to confirm SAM formation. In the case of 1-hexadecan, phenylacetylene, 1-undecanol, there were no oxidized Si peaks in XPS. This indicates that densely packed monolayers were formed so that the Si substrates were protected from oxidation. However, in the case of the other precursors, the Si substrates oxidized showing that such monolayers were less densely packed.¹ ² N. Saito, S. Youda, K. Hayashi, H. Sugimura and O. Takai, Chem. Lett. 31, 1194 (2002).

NS-TuP26 Fabrication of Cylindrical Cu Nanorods on an Indium-Tin-Oxide Substrate, S. Asakura, K. Oda, Waseda University, Japan; **A. Hozumi,** National Institute of Advanced Industrial Science and Technology, Japan; **A. Fuwa,** Waseda University, Japan

Increasing attention has recently been paid to the fabrication of copper (Cu) arrays of nm-scale in order to realize an ultrahigh-density electron emission source. Among the several methods, the use of diblock copolymer (BC) thin film is promising, since an ordered nanoporous structure can be easily obtained from the copolymer thin film by chemical treatment. Here we report the fabrication of cylindrical Cu nanostructures onto an indium-tin-oxide (ITO) substrate through an electrodeposition using a BC thin film as a template. First, a mixture of polystyrene (PS, 70 wt.%) / polybutadiene (PB, 30 wt.%) BCs and dehydrated toluene was stirred for 2 h at room temperature. Next, the solution was spin-coated on the ITO surface and dried in air for 24 h at a temperature of 140 °C. Due to this treatment, the PB component formed cylindrical domains in a matrix of the PS component as confirmed by an optical microscope. Subsequently, the sample was photoirradiated with vacuum ultraviolet (VUV) light of 172 nm in wavelength for 30 min at 10³ Pa. As a control experiment, identical BC thin film/ITO sample was sonicated in dehydrated toluene for 30 min. Finally, each sample was treated in an electroplating solution to deposit Cu on it. Using a scanning electron microscope, we confirmed that the Cu deposition selectively occurred inside the cylindrical nanopores where the PB domains were photochemically eliminated. The cylindrically shaped Cu nanorods on the ITO surface were less than 800 nm in diameter and several hundreds nm in length. Our result presented here

demonstrated that the PB domains were removed completely due to VUV irradiation and the PS matrix served as a mask to prevent Cu deposition. On the other hand, in the case of the chemical treatment, no Cu deposition was observed. This indicates that the PB domains still remained on the ITO surface. Our VUV treatment was found to be effective for preparing the nanoporous structures in the BC thin film.

NS-TuP27 Organic Self-Assembled Monolayers Covalently Linked to Diamond Electrode Surfaces, R. Ohta, N. Saito, Y. Inoue, H. Sugimura, O. Takai, Nagoya University, Japan

Diamond has excellent properties as an electrode material for electrochemical sensors, besides its well-known properties as the hardest material in nature. It has a wide potential window and chemical stabilities in various environments. Chemical functionalization of diamond surfaces is a powerful means in order to provide chemical selectivity and sensitivity to the diamond surfaces. Thus, it is a crucial technique for developing diamond-based chemical sensors. However, in actual applications of a modified diamond electrode, its surface is needed to be durable chemically and mechanically. Organic molecular monolayers covalently linked to diamond surfaces meet these demands and promising candidates. In this research, we have studied both vapor phase and liquid phase processes for the modification of hydrogen-terminated diamond to several organic molecules such as 1-undecanol and 1-hexadecan as well as that of hydroxyl-terminated diamond to organosilane molecules such as alkylsilane and aminosilane. The molecules were fixed onto the diamond surfaces through covalent bonds such as C-O-C, C-C and C-O-Si and consequently formed self-assembled monolayers. The monolayers were characterized by scanning probe microscopy, X-ray photoelectron spectroscopy and infrared spectroscopy. These results will be discussed with the electrochemical behavior of the modified-diamond surfaces. Micropatterning of the diamond surfaces will be also presented.

NS-TuP28 Photochemical Reaction of Organosilane Self-Assembled Monolayers as Studied by Scanning Probe Microscopy, H. Sugimura, N. Saito, I. Ikeda, Y. Ishida, K. Hayashi, O. Takai, Nagoya University, Japan

Photopatterning of organosilane self-assembled monolayers has attracted attention due to a wide variety of applications of micropatterned monolayers as micro templates for immobilizing biomolecules, nanoparticles, polymers and so forth. For such advanced applications of the micropatterned monolayers, the study on photochemical reactions proceeding on the monolayers due to photo irradiation is indispensable. In this study, we used two types of the monolayers prepared on Si substrates from octadecyltrimethoxysilane (ODS) and chloromethylphenyltrimethoxysilane (CMPHS). Each monolayer was micropatterned by irradiating the monolayer through a photomask with a light at 172 or 244 nm in wavelength in the presence of atmospheric oxygen molecules. Although, the CMPHS monolayer could be micropatterned by both the light at 172 and 244 nm, patterning of the ODS monolayer was capable only by the light at 172 nm. Generation of activated oxygen atoms through the excitation of the atmospheric oxygen molecules had a crucial role in photopatterning at 172 nm, while excitation of aromatic rings was the key process for patterning of the CMPHS monolayer at 244 nm. Photochemical reactions proceeded on the monolayers were further studied in minute scale through changes in friction and surface potential due to photo-irradiation by means of scanning probe microscopy, that is, lateral force microscopy and Kelvin-probe force microscopy, respectively. These results will be discussed with results obtained from spectroscopic studies such as X-ray photoelectron and infrared absorption spectroscopies.

NS-TuP29 Self-organizing Processes in Connection with Nanocluster States, W. Schommers, M. Rieth, Forschungszentrum Karlsruhe, Germany; **S. Baskoutas,** University of Patras, Greece

In the past experimental as well as theoretical investigations have shown that the structure of metallic nanoclusters most often deviates significantly from those of the bulk. With the help of molecular dynamics calculations we demonstrate how the transition from bulk structured materials to nanostructured clusters might take place, e.g., during a production process. In connection with such structural transitions one result is rather interesting: the occurrence of meta-stable cluster states. The conditions under which such meta-stable nanostructures might be possible and how their life-time could be influenced is systematically investigated. Such structurally meta-stable atomic compounds are commonly known in connection with huge complicated inorganic molecules. Especially in biology such meta-stable molecules are most often observed to store energy or to act as propulsion system in one way or another by changing

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parts of its structure. Our molecular dynamical investigations have shown that specific metallic nanoclusters behave similar. In this connection we also tried to answer the following questions: How is the dynamics of nanoclusters changed when they transform from the metastable to the stable state? Is this behavior restricted to specific materials? And what is the underlying mechanism?

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