Processing at the Nanoscale/NANO 6
Room Exhibit Hall C & D - Session NS+NANO6-WeP
Poster Session

NS+NANO6-WeP1 Nanometer Atomic Layer Growth and Removal from Surfaces of Inorganic Single Crystals: Scanning Probe Microscope Studies Under Controlled Solutions*, **J.T. Dickinson**, R. Hariadi, S.C. Langford,* Washington State University

Using the tip of a Scanning Force Microscope in solutions with controlled ionic content, we combine the application of single asperity forces to aquous surfaces of inorganic single crystals. With appropriate combinations of reactivity and stress, we are able to locally remove or deposit crystalline material in atomic layers and dimensions of nanometers. We show for the first time that layer by layer crystal growth can be controlled mechanically in such a fashion that fills in micron-sized features a few atomic layers deep. The recrystallization is done under supersaturated solution conditions. Step edges are stimulated with low contact force scanning using a scanning force microscope (which is also used to image the changes in surface topography. We present recent results on single crystal brushite (CaHPO@sub4@.2H@sub2@O) where we find strong dependencies on solution chemistry, mechanical parameters (e.g., normal force), and step crystallography. A model for both material removal and deposition will be presented. These studies allow production of nanoscale structures and atomically flat surfaces under low temperature conditions.

NS+NANO6-WeP2 Attractive Mode Molecular Manipulation at Room Temperature*, M.J. Humphry, **P.H. Beton**, P. Moriarty,* University of Nottingham, UK

We have investigated the manipulation of C60 on Si(100)-2x1 using the tip of a scanning tunneling microscope (STM) operating ultra-high vacuum at room temperature. During repulsive manipulation the tip follows a quasi-periodic trajectory as the molecule is displaced through integer multiples of the surface lattice constant and the tip is partially retracted during the manipulation process. A clear voltage threshold and characteristic tip response for this mode of manipulation is established. In addition molecules are observed to move through a displacement of up to three lattice constants (1.1nm) towards the STM tip due to an attractive interaction. This effect is observed over a wide range of tunneling parameters and is related to 'streaking' in STM images in which molecules may be dragged across the Si surface. The mechanism for this behaviour will be discussed together with the potential for the controlled assembly of molecular nanostructures.

NS+NANO6-WeP3 Manipulation of Single Cu-TBPP Molecules by Low Temperature STM*, **F. Moresco**, G. Meyer, K.H. Rieder,* FU Berlin, Germany*; H. Tang, A. Gourdon, C. Joachim,* CEMES CNRS Toulouse, France

The development of integrated nanoelectronic devices and the requirement of assembling perfectly identical nanostructures has recently focused the research attention on the vast range of possibilities offered by molecular structures. Controlled positioning of individual molecules can be performed by lateral manipulation with the STM tip. STM is in this respect a very promising technique because it contemporarily allows to determine the structure and conformation of the molecules and to build controlled molecular nanostructures without affecting the internal structure of the molecules. A detailed investigation of the processes involved in the manipulation of individual porphyrin-based molecules by scanning tunneling microscopy at low temperature is presented. The molecular conformation on different Cu surfaces is discussed. We show that the molecules occupy different configurations, depending on the interaction with the substrate and on the orientation of the four lateral substituent groups. By means of vertical and lateral manipulation it has been possible to switch between the different conformations and to exploit in detail the interaction between the STM tip and the molecule. Due to the complicated structure of the molecules we have explored different manipulation techniques, exploiting not only constant current but also constant height lateral manipulation.

NS+NANO6-WeP4 Nanolithography on Silicon Surface using a Tuning-fork STM/AFM*, **S.Y. Lin**, S.C. Yang, J.-D. Su,* National Taiwan University*; D.P. Tsai,* National Taiwan University, Taiwan*; F.S.-S. Chien, S. Gwo,* National Tsing-Hua University, Taiwan*; W.-F. Hsieh,* National Chiao-Tung University, Taiwan

A tapping-mode atomic force microscope (AFM)/scanning tunneling microscope (STM) system using a non-optical tuning fork force-sensing method has been developed for the scanning probe lithography. Comparing with the nano-lithography done by the AFM having the conductive cantilever tip, our method has the following advantages: (1) It has longer tapered length STM tip and smaller half cone angle to perform the nanometer scale patterning with high aspect ratio. (2) Its low cost tungsten or Pt/Ir STM tip can be easily fabricated and attached to our AFM force-sensing tuning fork. (3) It can be easily adapted to large-scale parallel processing because of the all-electric force-sensing method. Nanostructures with high aspect ratios and large depths have been successfully performed on the silicon surfaces by using our AFM/STM nano-patterning system followed by the differential etching process. Lines with different widths and matrix of dots with various diameters were demonstrated for potential applications.

NS+NANO6-WeP5 Etching of GaN (0001) with Halogens: Pit Growth and Step Etching by Cl*, **K.S. Nakayama**, S. Kuwano, Q.Z. Xue,* Tohoku University, Japan*; Q.K. Xue,* Chinese Academy of Science*; T. Sakurai,* Tohoku University, Japan

We have studied the etching of GaN (0001) by Cl using scanning tunneling microscopy (STM) to obtain morphological information that can be related to surface reaction and desorption pathway. We used N- and Ga- polar GaN surfaces prepared by N-plasma-assisted molecular beam epitaxy (MBE) followed by Ga deposition. A Ga rich GaN(0001) surface was exposed to molecular Cl@sub 2@ at room temperature for the coverage of more than 1 monolayer. Heating to 600-700 °C induced etching by thermal desorption. STM images show that smooth and rough steps appeared and these triangle pits were initiated on the terrace after the thermally activated reaction. The height profiles of a pit and a step in the STM images reveal layer-by-layer removal of GaN. The etching directions of steps can be attributed to the number of dangling bond at the step edges. We also discuss possible desorption pathways with atomic scale including the formation of volatile GaClX products and the spontaneous desorption of nitrogen molecule. When the Ga atom on the top layer removed by Cl, the nitrogen atom in the second layer appeared having two dangling bonds. This configuration would be energetically unfavorable and the distance of dangling bonds of neighboring nitrogen atoms is very close. Therefore, the nitrogen atoms would combine each other to form nitrogen molecules and the spontaneous desorption would occur on the surface.

NS+NANO6-WeP6 Adsorption of Benzene and Pentacene on Metal Surface: A Scanning Tunneling Microscope Study*, J.-Y. Park, Y.-J. Song, **Y. Kuk**,* Seoul National University, Korea

A single benzene molecule is known to have three different shapes in scanning tunneling microscope(STM) image depending on the adsorption sites. The ordered benzene layer and the (3X3) benzene layer coadsorbed with carbon monoxide on Pd(111) are studied with STM. It is revealed that the ordered benzene layer can transform to the disordered layer with temperature or defects on substrates, suggesting the small heat of adsorption. The (3X3) benzene layer coadsorbed with carbon monoxide on Pd(111) is more stable than that without carbon monoxide. Unusual phase boundary was found at every other benzene rows, suggesting elastic strain in the layer. On the other hand, pentacene is known as a candidate for organic device. The adsorption and electronic structure of pentacene, adsorbed on Cu(111) surface, is also investigated with STM. The electronic and geometric contribution to STM image will be discussed with temperature dependent scanning tunneling spectroscopy data.

NS+NANO6-WeP7 Substrate-Directed Self-Assembly of Rigid Metallodendrimers*, **J.C. Poler**,* University of North Carolina, Charlotte

The subject of our research is the study of rigid dendrimer molecules, assembled on surfaces. Dendrimers are a class of molecule synthesized from repeating units such that the molecular topology is self-similar. A new class of geometrically rigid metallodendrimers has been synthesized recently by MacDonnell et al., and is enantiopure. These multinuclear molecules with Ru2+ centers are planar with D3 symmetry. We shall present AFM images of the self-assembled dendrimers on functionalized and patterned surfaces. Because these dendrimers are charged we can direct their self-assembly with electrostatic interactions at the surface.

Theoretical, molecular mechanics and experimental support for this process will be described.

NS+NANO6-WeP8 Amino-Terminated Self-Assembled Monolayer on SiO@sub 2@ Surfaces Formed by Chemical Vapor Deposition*, **A. Hozumi,*** National Industrial Research Institute of Nagoya, Japan*; H. Sugimura,* Graduate School of Nagoya University, Japan*; Y. Yokogawa,* National Industrial Research Institute of Nagoya, Japan*; K. Hayashi,* Graduate School of Nagoya University, Japan*; T. Kameyama,* National Industrial Research Institute of Nagoya, Japan*; O. Takai,* Graduate School of Nagoya University, Japan

In order to immobilize polymers, neurons, DNA and proteins etc., amino-terminated self-assembled monolayers (SAMs) have been applied. Although chemisorption of aminosilanes at the solid/liquid interface were studied extensively, there have been few reports on preparing aminosilane SAMs from vapor phase. Here, we report on the formation of an amino-terminated SAM on SiO@sub 2@/Si sample substrates on the basis of chemical vapor deposition (CVD). Cleaned SiO@sub 2@/Si substrates were exposed to vapor of aminosilane, that is, N-(6-aminohexyl)-aminopropyltrimethoxysilane (AHAPS) diluted with dehydrate toluene. Following CVD, these samples were washed by a successive immersion in dehydrate ethanol, dehydrate toluene, NaOH (1mM) and HNO@sub 3@ (1mM). This washing process was repeated several cycles. Finally, they were rinsed with MilliQ water and then blown dry with a N@sub 2@ gas stream. We have investigated in detail chemical and electokinetic properties of this amino-terminated SAM. The SiO@sub 2@/Si surface after CVD became hydrophobic showing a water-contact angle of ca. Thickness of the AHAPS-SAM was ca. 1.3 - (±)0.1 nm as estimated by ellipsometry. This value is comparable to the theoretical molecular length of AHAPS, i.e., 1.4 nm. As confirmed by AFM, the surface was very smooth and homogeneous with its roughness being almost identical to that of the SiO@sub 2@/Si substrate. Zeta-potentials of the AHAPS-SAM covered SiO@sub 2@/Si substrate were measured as a function of pH by means of an electrophoretic light scattering spectrophotometer. The surface was charged positively below its isoelectric point of pH 7-8, since the amine groups are easily protonated. Furthermore, we demonstrated micropatterning of the AHAPS-SAM based on the photolithography using an excimer lamp radiating vacuum ultra violet light of 172 nm in wavelength.

NS+NANO6-WeP9 Formation of Ferroelectric Nano-domains using Scanning Force Microscopy for the Mass Storage System*, **H. Shin,*** Samsung Advanced Institute of Technology & CRI, Korea*; J.G. Shin, S. Hong, J.U. Jeon,* Samsung Advanced Institute of Technology, Korea*; J. Woo, K. No,* Korea Advanced Institute of Science and Technology

Applying voltage between the conductive tip in atomic force microscope (AFM) and Pb(Zr,Ti)O@sub 3@ (PZT) films can cause the switching of ferroelectric domains in nanometer scale. Ferroelectric domains (less than 100 nm in diameter) were induced and analyzed. Imaging of ferroelectric domains was achieved by piezoresponse of the PZT films in contact mode of AFM with lock-in amplifier. De-convolution of the first harmonic signal from the lock-in amplifier reveals the details of the formation of nano domains in ferroelectric thin film materials. Formation and imaging of ferroelectric domains in nano size can be applicable to develop the future mass storage system with miniaturization and integration of the AFM through MEMS technology. In this paper, relevant issues, i.e. bit (induced ferroelectric domains) size dependence on poling voltage, pulse width, and film's thickness and microstructure as well as retention characteristics of the induced bits are discussed. In detail, the bit size showed a log-linear dependence on the pulse width and a linear dependence on the pulse voltage. Using the calculation of electric field distribution the size of the induced bits under certain pulse voltage and width was estimated and confirmed by the experiments. As a result it is clear that the thinner films are beneficial to induce smaller and more stable bits under the same poling voltage and pulse width. In addition retention loss phenomena of the induced ferroelectric domains were observed and carefully investigated. The retention loss can be described by an extended exponential decay which implies a narrow distribution of the relaxation times of the domains. Characteristic relaxation time was largely dependent upon poling time, domain size as well as film's microstructures. Finally, an effective way to improve retention failure of the induced ferroelectric domains was proposed and confirmed by experiments.

NS+NANO6-WeP10 Nanostrands of Poly(carbamatepropylsiloxane) on SiO2 Observed with Atomic Force Microscopy*, **H. Celio,** H. Cabibil, J. Lozano, J.M. White,* University of Texas at Austin

Poly(organosiloxane) polymers have recently received considerable attention due to their potential use as dielectric materials in advanced microelectronic applications. Using atomic force microscopy (AFM) and various spectroscopic methods (XPS, IR, Raman, SIMS), we have investigated the formation of linear strands of poly(carbamatepropylsiloxane) polymer (CPS) of nanoscale dimensions supported on native silicon oxide of Si(100). The CPS nanostructures were fabricated by the hydrolysis of @gamma@-aminopropylethoxysilane (@gamma@-APS) in a basic aqueous solution containing 3 @gamma@-APS: 1 K+ and excess CO@sub 2@. The CPS is deposited on SiO@sub 2@ by a spincoating procedure. The CPS nanostrands have lengths greater than 1000 nm, heights between 2 to 3 nm and widths on the average of ~10 nm. These strands are stable under ambient conditions for weeks. The linear directionality of these structures is dependent on the following parameters: 1) K+ cations, 2) strong hydrogen bonding interactions between propyl-NHCOO- and -NH@sub 2@ groups. The former is responsible for the formation of linear Si-O-Si backbone and neutralization of the carbamate (NHCOO-) group, while the latter is responsible for the self-assembly of CPS strands.

NS+NANO6-WeP11 Solution Deposition and Surface Characterization of Supported Gold Clusters*, **C.C. Chusuei,** X. Lai, K.A. Davis, P.S. Bagus, D.W. Goodman, M.A. Omary, M.A. Rawashdeh-Omary,* Texas A&M University

Nanosized Au cluster agglomeration has been a long standing problem in the preparation of planar model catalyst systems. A novel Au/TiO@sub 2@ catalyst preparation method was investigated. Six-atom gold clusters (in the form of a Au@sub 6@(PPh@sub 3@)@sub 6@ colloidal suspension) was deposited onto a TiO@sub 2@(110) single crystal via CH@sub 2@Cl@sub 2@ solution. Scanning tunneling microscopy (STM) and spectroscopy (STS) revealed structures consistent with unagglomerated, single unit entities. Electron stimulated desorption (0.12 Coulombs/cm@sup 2@) was then performed. X-ray photoelectron spectroscopy, high resolution electron energy loss spectroscopy (HREELS) and STM showed evidence for removal of the triphenyl phosphine ligands. Band gap measurements from HREELS, STS and theoretical calculations suggest that metal/metal oxide support interactions affect the Au electronic structure.

NS+NANO6-WeP12 Optical and Structural Properties of Ball Milled Produced Small Si Particles Embedded into a Sol-Gel Matrix*, **F.J. Espinoza-Beltrán,** L.L. Díaz-Flores, J.M. Yañez-Limón,* CINVESTAV-IPN, México*; J. Morales-Hernández,* Programa de Posgrado de Ingeniería, UAQ, México*; A. Mendoza-Galván,* CINVESTAV-IPN, México*; J. González-Hernández,* CINVESTAV-IPN, México, Mexico

Nano and micrometric silicon particles have been introduced into SiO@sub 2@ matrix produced by the sol-gel method, using tetraethyl-orthosilicate. The small Si particles were produced by grinding 99.999 % pure silicon granular polyfine in a low energy ball mill. The milling process, for various periods of time, was carried out in air conditions. For that reason, the small particles consist of a Si core surrounded by a SiO@sub x@ cap layer. According to infrared and Raman measurements, the Si core contains molecular structures of the form Si@sub n@, where n is in the range of 6 to 7. >From the position of TO IR active mode the value of x is estimated to be around 1.7. The silicon oxide cap also shows a strong LO mode, normally not observed at normal incidence in the IR absorption of planar SiO@sub 2@ thin layers. An IR line at about 630 cm@super -1@, also indicates that during the milling process, some atomic hydrogen is attached to the silicon particles. Sol-gel layers, with various Si particle sizes and various particle densities were prepared. The structural and optical properties of the as-prepared and heat treated, in the range of 100 to 800°C, powder and film samples were studied. The photoluminescence emission and optical absorption of the Si particles are related with their size and concentration.

NS+NANO6-WeP13 Fabrication of a Si Nanosize Pillar Array using Modified He/Cl2 Plasma Etching Process*, **J.W. Kim,** M.Y. Jung, D.W. Kim, S.S. Choi,* Sun Moon University, Korea

We have studied the effect of He flow rate on the dry etching process of Si and SiO2 layers using chlorine-based plasma. Experiments were performed using reactive ion etching system in order to fabricate a nanosize Si structure. The ion damage on the etch mask during etching process would hinder deeper and controllable etch profile. Rather than Ar gas, a He feed gas with Chlorine etch gas was exploited in order to reduce the ion damage. We have examined various etching characteristics of the He/Cl2 plasma and applied to fabrication of a Si pillar arrays. In this study, the fabrication of the Si pillar array with 5 micrometer height was successfully fabricated with 500 nm thickness electron beam resist only. We also fabricated the 10 micrometer deep Si trench with this modified He/Cl2 reactive ion etching system.

NS+NANO6-WeP14 A Novel Low Temperature Synthesis Route for Silicon Nanowires*, **S. Sharma**, M. Sunkara,* University of Louisville*; E.C. Dickey,* University of Kentucky*; R. Miranda,* University of Louisville

In this paper, we present a novel synthesis route for growing silicon nanowires at temperatures lower than the temperatures required for traditional vapor-liquid-solid (VLS) approaches that employ transition metals as catalysts. In the present work, gallium, which has low melting temperature (~30 °C) and broad temperature range for the melt phase (30-2400 °C at 1 atm), was used as a catalytic media for the low-temperature synthesis of silicon nanowires. Growth of silicon fibers was observed when silicon substrates covered with a thin film of liquid gallium, were exposed to a mixture of nitrogen and hydrogen in a microwave-generated plasma. The resulting silicon wires ranged from several microns to less than ten (10) nanometers in diameter. The observed growth rates were on the order of 100 microns/hr. Results indicate that this technique is capable of producing oriented rods, whiskers and with reasonable size distribution. We will present results showing the crystallinity, composition, patternability, and role of gas phase composition, obtained when using this technique. The growth mechanism in this method is hypothesized to be similar to that in other VLS processes, i.e., rapid dissolution of silicon hydrides in gallium melt, which catalyzes subsequent precipitation of silicon in one dimension in the form of wires. We believe that this technique offers several advantages over the conventional VLS technique using silicon-gold eutectic for catalyzed growth. In this technique, there is no need to supply silicon through the gas phase. Secondly, this technique in principle can operate at very low temperatures (<400 °C) thus allowing easier integration with other processing techniques and materials involved in electronics and opto-electronic device fabrication. Nanometer scale one-dimensional silicon structures such as nanowires and nanowhiskers are expected to be critically important in the future mesoscopic electronic and optical device applications.

NS+NANO6-WeP15 Fabrication of a Nanosize Oxide Aperture Array Coated with Thin Metal Films*, **J.W. Lee**, J.W. Kim, M.Y. Jung, D.W. Kim, S.S. Choi,* Sun Moon University, Korea

There have been considerable interests about the fabrication of the nano-size hole due to the potential application of the near field optical sensor or liquid metal ionsource. The 2 micron size dot array was initially patterned. After formation of the V-groove shape by anisotropic etching, dry oxidation was followed. In this procedure, the orientation dependent oxide growth was performed to have an etch-mask for dry etching. The reactive ion etching by the inductively coupled plasma system was performed in order to etch 90 nm silicon dioxide layer at the bottom of the V-groove and to etch the Si at the bottom. The negative ion energy on the bottom substrater would enhance the anisotropic etching by the Cl2 gas. After etching, the remaining thickness of the oxide on the Si(111) surface was measured to be 130 nm by scanning electron microscopy. After bulk micromachining from the backside Si wafer, the etched oxide aperture will be coated with metal thin film in order to improve the light trasmittance efficiency.

NS+NANO6-WeP16 Resolution Enhancement in Kelvin Probe Force Microscopy*, **R. Shikler**, O. Kazael, Y. Rosenwaks,* Tel-Aviv University, Israel

Kelvin probe force microscopy (KPFM) has become in recent years a valuable tool for characterizing and analyzing semiconductor surface electronic properties with nanometer resolution. The Kelvin probe force microscope measures the semiconductor work function by nullifying the electrostatic force between a vibrating tip and the semiconductor surface. It is accepted that the finite tip size in scanning probe microscopy can have a profound effect on the obtained topography image. This phenomenon is enhanced in KPFM measurements because the electrostatic force is long range, hence introducing topographic artifacts into the contact potential difference image. We propose an algorithm that improves the lateral resolution and reduces the topographic artifacts of the contact potential image by taking into account the full tip shape and the semiconductor surface. By using the real tip shape and sample topography (obtained using conventional blind tip estimation and dilation algorithms), the true contact potential difference image can be deconvoluted. A comparison of measured and deconvoluted KPFM images is presented, and the limits of the method are discussed.

NS+NANO6-WeP17 Effect of Beam Parameters in Electron Beam Induced Deposition of Rhodium from a Carbon Free Precursor: A Systematic Study*, **F. Cicoira**, I. Utke, P. Hoffmann, B. Dwir, K. Leifer, E. Kapon, D. Laub, H.J. Mathieu,* Swiss Federal Institute of Technology Lausanne, Switzerland*; P. Doppelt,* Ecole Superieure de Physique et Chimie Industrielle, Switzerland

Electron-beam induced deposition (EBID) offers unique advantages over classical resist-based processes, like the capability of depositing in situ conducting or dielectric materials, high aspect ratio supertips, air-bridges and other three dimensional structures. In our deposition system, based on a Cambridge S100 SEM with a thermionic tungsten filament, EBID is obtained by decomposing with the focused electrons a metal precursor directed to the sample surface by an internal needle. Carbon-free precursors are used to improve the purity of the EBID metal containing deposits. The inorganic precursor [RhCl(PF@sub 3@)@sub 2@]@sub 2@ allowed the deposition of nanocrystalline Rh containing supertips and nanowires with diameters down to 200 nm. Auger Electron Spectroscopy (AES) measurements show that the Rh deposits contain up to 60% of Rh. The rest of the deposit consists in P, Cl, N and O; no carbon could be detected after removal of the contamination layer. These results are confirmed by TEM investigation, revealing that the deposits have a crystalline structure and are covered by an amorphous 10-20 nm thick shell. TEM images allow also the determination of the Rh cluster size, which depends on the beam parameters used to induce the deposition and show that crystalline lines and tips with high Rh content can be obtained even when low deposition currents (some pA) are applied. In this work, we present a systematic study of the effect of the beam parameters on the properties of the deposits. Different two and three-dimensional structures have been deposited from the same precursor varying the electron energy, the electron current and the scanning speed of the electron beam. The obtained deposits have been characterized by Auger Electron Spectroscopy and Transmission Electron Spectroscopy to determine the chemical composition and the nanostructure for every set of parameters.

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