Thursday Morning, October 5, 2000

Processing at the Nanoscale/NANO 6 Room 302 - Session NS+NANO6-ThM

Nanostructured Materials

Moderator: T. Michalske, Sandia National Laboratories

8:20am NS+NANO6-ThM1 Implantation and Pinning of Size-selected Ag Nanoclusters at the Graphite Surface, S. Pratontep, S.J. Carroll, M. Streun, P.D. Nellist, R.E. Palmer, The University of Birmingham, UK; S. Hobday, R. Smith, Loughborough University, UK

Size-selected nanoclusters provide building blocks for creating nanoscale structures. However, the deposition of such clusters on surfaces is often susceptible to surface diffusion and thus aggregation of clusters. We have investigated the deposition of size-selected Ag@sub N@@super +@ clusters (N=20-200) on graphite at elevated impact energies (E=0.25-6 keV). Molecular dynamics simulations establish two energy regimes in which lateral diffusion of the deposited clusters is inhibited.@footnote 1@ At high impact energies (> 20 eV/atom) the clusters are found to penetrate into the surface and come to rest at the bottom of an open tunnel so created. The implantation depth is found to vary linearly as E/N@super 2/3@. This implies a constant decelerating force which is proportional to the cross-sectional area, rather than the volume, of the cluster. At lower impact energies (~10 eV/atom) we have found a size-dependent threshold energy above which the cluster is pinned on the surface at the impact site via the creation of a point defect. This threshold exhibits a linear dependence with the cluster size, N. This prediction is confirmed by scanning tunnelling microscopy (STM) investigations of cluster pinning as a function of cluster size and impact energy. Both the implantation and the pinning behaviour suggest viable methods for the fabrication of welldefined nanostructured surfaces. @FootnoteText@ @footnote 1@ S.J. Carroll, P.D. Nellist, R.E. Palmer, S. Hobday and R. Smith, Phys. Rev. Lett. 84, 2654 (2000).

8:40am NS+NANO6-ThM2 Self-organization of Pt Nanoparticles on Surfaces in Catalytic Reaction, *Q.-H. Hu*, *B. Kasemo*, Chalmers University of Technology, Sweden

Small metal particles have long been used as catalysts in heterogeneous catalytic reactions. The carrier may act both as a physical support and promoter for the catalytic reactions. Recently it is realized in the Monte Carlo simulation that supported cat alyst particles may self-organize through a rather complex interaction with the supported surface and gaseous species in the reaction environment. As consequence, individual particles may attain different shape(adsorbate-induced reshaping or facetting) an d combination of facets that strongly influence the reaction kinetics. In addition, particles as a whole may adopt different spatial arrangement, which affects mass-transport in the reaction. We report a technique for preparing SiN-membrane and TEM observ ations of selforganization of Pt nanoparticles on the membrane in the catalytic reaction. The TEM of as-prepared samples 'Pt deposited on the membranes' showed three types of morphology, continuous granular film at the nominal thickness of above 20 nm, irr egular-shaped drops of varied sizes and coverage below 5 nm, and semi-continuous films with varied density of cracks at the thickness in between. The TEM of the samples heat-treated in the ambience of H2 and O2 at atmospheric pressure showed significant c hange in morphology. Thin Pt samples treated at 300 °C and H2/O2=0.4 self-organized into short-range ordered nanoparticles of less than 5 nm in size with a comparable interparticle spacing. The particle size is proportional to the initial thickness. On the medium thickness samples, multi-connected irregular-shaped islands resulted. The width of the interconnection is about 10 nm and almost equal to the spacing between the islands. Recrystalization of Pt was also observed. A systematic variation of treatment conditions on samples of different thickness, together with the evaluation of the catalytic activity is currently undertaken to realize a controlled shape of the self-organized particles.

9:00am NS+NANO6-ThM3 Quantum-Coherence and Self-Assembly of Metallic Nanostructures, H. Brune, Ecole Polytechnique Federale de Lausanne, Switzerland INVITED

We will discuss several means for the self-assembly of metallic islands of well defined size and mutual distance. The surface states of the (111)oriented transition metal surfaces have extremely small Fermi vectors leading to long wavelength quantum-interference patterns. For Cu/Cu(111) these Friedel oscillations give rise to long range oscillatory adsorbateadsorbate interactions which can be used to arrange adatoms or islands in hexagonal patterns. The period of these superlattices is @lambda@@sub F@/2 and thus coherently reflects the surface electronic properties. We then present the growth of nanostructure arrays using kinetically controlled growth on dislocation networks serving as templates. The mean size of the Ag, Fe, and Co dots is adjusted by the coverage. Their size distribution is given by the statistics of deposition. It has a half width at half maximum of 12% at 0.10ML, which is competitive with state-of-the-art semiconductor quantum dots, and goes down to 4% at 0.5ML. Small Co islands with well defined sizes can be created through coarsening by cluster diffusion on Pt(111). Since each cluster size has its own onset temperature for diffusion one can deliberately adjust the mean island size by the annealing temperature giving rise to high densities of very small islands ideally suited to investigate size-effects on reactivity and magnetic moment per atom.

9:40am NS+NANO6-ThM5 Immobilization and Isolation of Molecule Corral Nanostructures Produced on Highly Oriented Pyrolytic Graphite, J.D. McBride, Y.J. Zhu, B. Van Tassel, R.C. Jachmann, T.P. Beebe, Jr., University of Utah

Gold and silver nanostructures have been produced by condensing evaporated gold onto nanometer-sized etch pit templates (molecule corrals) on the surface of highly oriented pyrolytic graphite (HOPG). By varying the ratio of the thickness of gold deposited to the diameter of the etch pit templates, three distinct types of gold nanostructures can be produced: rings, disks, and mesas. These nanostructures have been formed with their outer diameters ranging from 20 to 150 nm. In order to use these nanostructures in the microelectronics industry, or for potential use as sensor arrays, they must be isolated both from one another as well as from the conductive graphite surface on which they are produced. Two different methods for isolating these nanostructures have been investigated. First, the use of (3-mercaptopropyl)trimethoxysilane (MPS) as a molecular adhesive@footnote 1@ to anchor the gold nanostructures to glass and silicon substrates was evaluated. The degree of gold transfer to the glass and silicon surfaces was examined using x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning tunneling microscopy, and atomic force microscopy. The second technique used for isolating gold nanostructures was the immobilization and encapsulation of the nanostructures within a spincoated fluoropolymer film. These polymer films were examined using both the spectral and imaging modes of XPS and ToF-SIMS. @FootnoteText@ @footnote 1@ Goss, C. A.; Charych, D. H.; Majda, M. Anal. Chem. 1991, 63, 85-88.

10:00am NS+NANO6-ThM6 Ultraflat Nanosphere Lithography, W. Frey, A. Chilkoti, Duke University

Easy fabrication of periodic features on the submicron scale is needed for many applications ranging from surface-enhanced spectroscopy to quantum structures and nanostructured biofunctional surfaces. For example, biosensors require nanopatterns to be stably bonded to the substrate in solvents, as well as capable of subsequent functionalization by self-assembly chemistry. Additionally, for the study of cell surfaceinteractions, the nanopatterned surface should have minimal height variation in order to decouple physico-chemical and topographical effects on cell behavior. We have therefore designed a new method, ultraflat nanosphere lithography (UNSL), to create periodic nanopatterned surfaces of well-defined size and minimal topography for different materials that are also stably bonded and are capable of self-assembly chemistry. UNSL is based on nanosphere lithography@footnote 1@ and ultraflat template stripping.@footnote 2@ Nanospheres are self-assembled into close packed hexagonal arrays on mica. Material M1 is evaporated through the mask formed by the self-assembled spheres. After the spheres have been lifted off the substrate, evaporation of material M2 embeds the nanopattern in a much thicker matrix. A silicon or glass substrate is glued to the surface for mechanical support. Finally, the mica is stripped off, revealing an ultraflat pattern of nanotriangles of M1 embedded in M2. In order to demonstrate the feasibility of UNSL, we have chosen pairs of materials M1 (Au, Ag) and M2 (Al, SiO) so that each can be independently functionalized by orthogonal self-assembly, and transparent samples as well as insulatorconductor pairs can be created. We have visualized the nanopatterns fabricated by UNSL using AFM, SEM and Auger electron imaging, and demonstrate that the surface roughness is below 1 nm (rms) over areas of several hundred µm@super 2@. @FootnoteText@ @footnote 1@Deckman, et.al.: Appl. Phys. Lett. 41, 377 (1982)@footnote 2@Hegner, et.al.: Surf. Sci. 291, 39 (1993)

Thursday Morning, October 5, 2000

10:20am NS+NANO6-ThM7 Controlled Growth of Metal Nanoclusters on Polymers, V. Zaporojtchenko, K. Behnke, A. Thran, T. Strunskus, F. Faupel, University of Kiel, Germany

Metal nanoparticles dispersed on a polymer surface as well within a polymeric matrix offer interesting electronic. optical and catalytic properties due to their small dimensions.@footnote 1@ For metals with moderate reactivity the high cohesive energy of the metal in combination with the weak metal-polymer interaction leads to metal aggregation on the surface. The nucleation and growth of noble metals (Cu, Ag, Au) as well as more reactive metals (Ni, Cr) onto fully cured polymer films with different composition are considered. The metal deposits which were prepared in situ by physical vapor deposition were characterized by combination of transmission electron microscopy (TEM), atom force microscopy (AFM), xray photoelectron spectroscopy (XPS) and a novel very sensitive radiotracer technique.@footnote 2@ An extreme variation in metal condensation behavior was observed on the different polymers. It appears to be related to the polymer surface energy and suggests a connection between macroscopic wetting and atomic condensation. The effect of metalpolymer interaction as well as the deposition parameters and surface pretreatment on the nucleation process has been investigated in order to understand how the morphology of the metal deposit can be affected. Influencing the basic processes@footnote 3@ occuring in the initial stages of metal-polymer interface formation it is possible to form 2-d metal nanoparticle-polymer composits with a large variation of the metal cluster size and metal cluster density on the polymer surface. @FootnoteText@ @footnote 1@ Metal Clusters, ed. by W. Ekardt, John Wiley & Sons, Chichester, England 1999. @footnote 2@ A. Thran, M. Kiene, V. Zaporojtchenko and F. Faupel, Phys. Rev. Lett. 82, 1903 (1999). @footnote 3@ V. Zaporojtchenko, T. Strunskus, K. Behnke, M. Kiene, and F. Faupel, J. Adesion Sci. Technol., 14(3), 467 (2000).

10:40am NS+NANO6-ThM8 Noble Metal Nanoparticles in Polymeric Thin Films, M.K. Chilton, P.G. Van Patten, Ohio University

Recent results obtained in our laboratory and elsewhere have demonstrated the possibility of using noble metal nanoparticles to enhance the emissive response from phosphor materials by more than an order of magnitude. We have employed electrostatically-grown polymer-based thin films as model systems for a series of experiments on these light-emitting nanocomposites. The fabrication and characterization of these model thin films will be described in detail along with spectroscopic results from the phosphor films. The enhancement effect has thus far only been observed in trivalent lanthanide ions. Experimental results suggest that the enhancement mechanism is related to the field focussing properties of the nanoparticles. Localized field enhancement apparently leads to the introduction of odd parity terms into the transition matrix element for photoabsorption. Interestingly, the rate of spontaneous emission from the ions are not observed to change as a result of the nanoparticles' presence. A detailed hypothesis for the mechanism will be presented consistent with existing photophysical evidence. The implications of the enhancement phenomenon for device development will also be discussed.

 11:00am
 NS+NANO6-ThM9
 Biomimetic
 Self-Assembly,
 G.
 Stucky,

 University of California, Santa Barbara
 INVITED

 PLEASE SEND US AN ABSTRACT.
 Thank you.

11:40am NS+NANO6-ThM11 Cluster Size Effect Observed for Gold and Silver Sulfide Nanoparticles Synthesized by Sol-Gel Technique as Studied by X-ray Photoelectron Spectroscopy, *S. Shukla*, *S. Seal*, University of Central Florida; *S. Mishra*, University of Memphis

Gold and Silver Sulfide nanoparticles have been successfully synthesized by a novel sol-gel technique. AFM analysis indicates the formation of @<=@12-14 nm and 40-60 nm size Au nanoparticles; while TEM and AFM analysis indicate the formation of Ag@sub 2@S nanoparticles with average size of 26 nm (with broad size distribution ranging from 2.5 nm to 56 nm) and 200-300 nm, for respective H@sub 2@S/not heated and H@sub 2@S/heated samples. XPS analysis of H@sub 2@S/not heated sample, for Au nanoparticles, reveals that the core-level Au 4f@sub 7/2@ B.E. is shifted by +0.3 eV (with increase in the FWHM of 0.2 eV) relative to the bulk value of 84.0 eV. The shift is interpreted in terms of the changes in the electronic structure due to finite cluster size and creation of +ve charge over the surface of cluster during the photoemission process itself. The electronic structure of Au nanoparticles (or clusters) produced via present sol-gel technique is compared with that of Au clusters deposited by evaporation method described in the literature. XPS analysis of Ag@sub 2@S nano and powder particles suggests that the Ag 3d@sub 5/2@ B.E. level is a function of particle size distribution. Moreover, in both the

systems, -ve shift in the core-level B.E. is observed, for H@sub 2@S/heated sample, which is attributed to the small size of the particles and their faceted nature. Suitability of the present method to produce silver sulfide ion-selective electrodes is demonstrated by depositing Ag@sub 2@S nanoparticles on the graphite rod and testing its response function.

Author Index

Bold page numbers indicate presenter

- B --Beebe, Jr., T.P.: NS+NANO6-ThM5, 1 Behnke, K.: NS+NANO6-ThM7, 2 Brune, H.: NS+NANO6-ThM3, 1 - C --Carroll, S.J.: NS+NANO6-ThM1, 1 Chilkoti, A.: NS+NANO6-ThM6, 1 Chilton, M.K.: NS+NANO6-ThM8, 2 - F --Faupel, F.: NS+NANO6-ThM7, 2 Frey, W.: NS+NANO6-ThM7, 1 Hobday, S.: NS+NANO6-ThM1, 1 Hu, Q.-H.: NS+NANO6-ThM2, 1

- J --Jachmann, R.C.: NS+NANO6-ThM5, 1 - K --Kasemo, B.: NS+NANO6-ThM2, 1 - M --McBride, J.D.: NS+NANO6-ThM5, 1 Mishra, S.: NS+NANO6-ThM1, 2 - N --Nellist, P.D.: NS+NANO6-ThM1, 1 - P --Palmer, R.E.: NS+NANO6-ThM1, 1 Pratontep, S.: NS+NANO6-ThM1, 1 - S --Seal, S.: NS+NANO6-ThM11, 2 Shukla, S.: NS+NANO6-ThM11, **2** Smith, R.: NS+NANO6-ThM1, 1 Streun, M.: NS+NANO6-ThM1, 1 Strunskus, T.: NS+NANO6-ThM7, 2 Stucky, G.: NS+NANO6-ThM9, **2** - T -Thran, A.: NS+NANO6-ThM7, 2 - V -Van Patten, P.G.: NS+NANO6-ThM8, **2** Van Tassel, B.: NS+NANO6-ThM5, 1 - Z -Zaporojtchenko, V.: NS+NANO6-ThM7, **2** Zhu, Y.J.: NS+NANO6-ThM5, 1