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The 3D Nanoengineered Assemblies symposium brought together researchers from a wide range of fields. The conference topic is not focused on a particular area of research, but on a goal that is being pursued by many groups approaching from diverse directions. 3D Nanoengineered Assemblies included much work that was "not quite truly 3D" and "not quite on the nanoscale." The result was a meeting in which common overarching themes emerged from presentations in widely separated research areas. More than 100 abstracts were submitted, and there were 29 invited talks covering work that spanned a remarkable number of topics. The symposium was generally well attended, and there was good feedback about the overall quality of the presentations.

One of the most interesting aspects of nanotechnology is the ability to access physical phenomena that occur on the nanoscale. A compelling example of this sort of nanoscale phenomena exploits the collective electronic excitations (plasma oscillations or plasmons) in metal nanoparticles to manipulate energy and matter. This work was well represented by talks from Harry Atwater (CalTech), Frank Traeger (Kassel), Mostafa El-Sayed (Georgia Tech), Richard Blaikie (Canterbury) and Meg Abraham (Aerospace Corp.). In particular, Harry Atwater's talk showed how plasmons in metal particles on a surface could be used to direct the flow of energy in a material analogous to more conventional electronic devices. Other talks demonstrated the use of plasmons to control the size and shape of the metal nanoparticles both on a surface and in the bulk. This is a compelling set of applications for nanotechnology in general and 3D nanoengineered assemblies in particular.

Lithographic methods can be either masked based or mask-less. Much of the time devoted to modern materials processing has been spent developing mask based lithographic techniques and as a consequence they are quite mature. Some of the speakers presented work that used conventional methods at high resolution to great advantage. An example of this sort of work is provided by the presentation of Harold Craighead (Cornell). There were a variety of talks that presented variations on these methods, perhaps best exemplified by Ulrich Gosele's talk (MPI-Halle). Steven Brueck (UNM) presented a talk on laser based interference methods that both argues that the limits to optical methods have not been reached. This connects with lithographic processes because nonlinear response is important both for photo resist materials and for many of the direct write schemes for processing in three dimensions, (such as found in the work of Shoji Marou and Koji Ikuta).

The mask-less direct write processing community was well represented by electron and particle beam talks including those of J. Alex Liddle (LBNL), Hans Loeschner (IMS), and Andrew Bettiol (Nat. U. Singapore). There were also a variety of talks on soft lithographic methods, including John Rogers (Lucent) and Sigurd Wagner (Princeton).

Non-lithographic techniques were also discussed in this meeting. This included a number of talks on self-assembly. Nanoparticle assemblies, Nanotubes, Nanowires and Nanosprings were the topics of a number of talks. Ones that stand out in my memory
are Reg Penner’s (UC Irvine) talk on electrochemical methods of producing nanowires, Walt deHeer’s (Georgia Tech) and Dave McClroy’s (U Idaho) nanospring talk.

Two of the aspects of the biological model for materials processing that make it most appealing are the directed self-assembly and the bottom-up approach to processing. Together, these aspects of biological control of materials have become a prototype for an elegant approach to processing. If biological processes can be understood and controlled or mimicked, then there is potential to build structures starting on the nanoscale. This approach implicitly offers some level of 3D control from the nanoscale all the way to large structures. A significant part of this work has been directed at carbonates and this was highlighted in an overview talk from Dan Morse (UCSB) and excellent talks from several speakers including Jim deYoreo (LLNL) and Ken Sanhage (Ohio State).

A large number of excellent talks presented interesting work in this symposium. Part of the success of the “3D Nanoengineered Assemblies” symposium is that it touches on a presently topical aspect of research. However, the real strength of this meeting was the multidisciplinary character of the entire symposium. I believe this was evident when a chemist and a physicist who might seldom cross paths gave related talks in the same session. This also happened in the “plasmon processes on the nanoscale” session where the collection of talks told part of a larger story concerning what I think is one of the most interesting examples of the sort of emerging new physics that can be accessed with control of materials on the nanometer scale. The “3D Nanoengineered Assemblies” symposium succeeded in presenting to researchers a snapshot of the current work on this topic, in keeping with the best traditions of the Materials Research Society Meetings.

David P. Taylor
The Aerospace Corporation
SYMPOSIUM H
Three-Dimensional Nanoengineered Assemblies
December 1 – 5, 2002

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TUTORIAL
FT H: LITHOGRAPHIC AND NONLITHOGRAPHIC METHODS FOR 3D NANOFABRICATION
Sunday, December 1, 2002
2:00 p.m. - 5:00 p.m.
Room 201 (Hynes)

Nanotechnology is considered the key technology of the 21st century and is expected to bring ultimate solutions to current problems. However, among the issues to address is the potential impact of nanotechnology, which is the selection of a 3D nanofabrication method that can be scaled up.

For more details, please refer to the attached text.

Instructors:
Shinji Matai, Hitachi, Ltd
John A. Rogers, Bell Laboratories, Lucent Technologies

SESSION III: NANOFABRICATION VIA LITHOGRAPHIC TECHNIQUES
Chaired by David M. Taylor and David P. Taylor
Monday Morning, December 2, 2002
Room 309 (Hynes)

8:30 AM "H1.1"
INTERFEROMETRIC LITHOGRAPHY AND NANOSCALE-PATTERNED SEMICONDUCTOR GROWTH, S.J. Brueck, Center for High Technology Materials, University of New Mexico, Albuquerque, NM.

Interferometric lithography (IL) provides a facile, large-area, low-cost nanopatterning technique. Using available ultraviolet laser sources, pattern periods as low as 25 nm are possible. Since the limitation in optics is on the period rather than the linewidth, nonlinear interband techniques allow extension to ≈70 nm and below. Interband techniques will be demonstrated.

9:00 AM "H1.2"
TECHNIQUES AND APPLICATIONS FOR NON-PLANAR LITHOGRAPHY, John A. Rogers, Bell Laboratories, Murray Hill, NJ.

Certain specialized techniques for high resolution printing and molding can be used to form micro and nanoscale structures directly onto non-planar (e.g., curved, multi-layered) surfaces. This talk describes some of these methods and discusses the current state of these techniques as well as future directions.

9:30 AM "H1.3"
ION PROJECTION DIRECT-STRUCTURING (IPDS) FOR NANOTECHNOLOGY APPLICATIONS, Hans Loescher, Einar Platssammer, and Gerhard Stengl, IMS Nanofabrication GmbH, Vienna, Austria.

Large-field ion-optics has been developed for reduction and proximity printing. The projection of patterned magnetic media has been demonstrated within exposure fields of 17mm diameter. Tool development and further improvements of the IPDS nanotechnology applications will be discussed.

10:00 AM "H1.4"
PROTON BEAM MICROMACHINING: A NEW 3D SUB-100 NM DIRECT-WRİTE TECHNIQUE, Frank Watt, Jeroen van Kan, and Bert Jelger, Research Centre for Nuclear Microscopy, Dept. of Physics, National University of Singapore, Singapore.

Proton Beam Micromachining (PBM) using MeV protons has the unique capability of producing direct-write high-aspect-ratio 3D structures in resist material. Proton beams, being 1800 times more massive than electrons, do not suffer from lateral scattering as the protons penetrate the resist and, unlike X-rays, have an almost linear energy deposition with depth (except for a localized increase at the end of range). These features allow smooth, straight-walled, high aspect ratio structures to be produced. An added feature is that the depth to which the protons expose the resist can be varied by changing the proton energy, allowing multi-level 3D structures to be created (e.g., a 1 MeV proton beam will penetrate 20 microns in PMMA, whereas a 2 MeV beam will penetrate 61 microns). Investigations taking place in the Research Centre for Nuclear Microscopy, Dept. of Physics, National University of Singapore, have shown that the PBM process has high potential for 3D applications in microelectronics, biomaterials, tissue engineering substrates, and is in particular suited to the rapid production of high quality 3D stamp and molds for soft lithography using polymers. In addition, recent advances in quadruple lens technology has enabled protons to be focused down to 36 nm spot sizes, enabling sub-100nm 3D structures to be produced.

11:00 AM "H1.5"
RESIST REQUIREMENTS AND LIMITATIONS FOR NANOSCALE ELECTRON-BEAM PATTERNING, J. Alexander Liddle, Lawrence Berkeley National Laboratory, Berkeley, CA.

Electron beam lithography still represents the most effective way to pattern materials at the nanoscale, especially in the case of structures, which are not indefinitely repeating a simple motif. The success of e-beam lithography depends on the availability of suitable resists. There is a substantial variety of resist materials, from PMMA to azo resists, to choose from to achieve high resolution in electron-beam lithography. However, these materials suffer from the limitations of ambient sensitivity. In both direct-write and projection e-beam systems the maximum beam current for a given resolution is limited by space-charge effects. In order to make the most efficient use of the available current, the resist must be as sensitive as possible. This leads, naturally, to chemically amplified (CA) systems. Unfortunately, in the quest for ever smaller feature sizes and higher throughputs, even chemically amplified materials are limited: ultimately, sensitivity and resolution are not independent. Current resists already operate in the regime of < 1 electron/μm². In this situation discrete models are the only way to understand material performance and limits. In this talk I will discuss resist requirements, including sensitivity, etch selectivity, environmental stability, outgassing, and line-edge roughness as they pertain to, high voltage (100 kV) direct write and projection electron-beam exposure systems. I will present some of the experimental results obtained on CA resists in the SCALPEL exposure system and discuss the fundamental sensitivity limits of CA and conventional materials in terms of shot-noise and resolution limits in terms of e-beam solid interactions.

11:30 AM "H1.6"
NANOSCALE PATTERNING OF COBALT-COBALT OXIDE INTERFACES, J.W. Luo, Y. Zhu, Brookhaven National Laboratory, Upton, NY.

A goal of this project is to tailor assemblies of Co/CoO structures for the purpose of evaluating magnetic behavior with ferromagnetic and antiferromagnetic interfaces. We have successfully patterned periodic structures containing cobalt-cobalt oxide interfaces with electron beam lithography. A 20 nm uniform cobalt film was deposited on both silicon nitride and holey carbon substrates. A 10 nm layer of aluminum was used as a diffusion barrier. The lithography procedure removes both aluminum and fluoriyne, leaving behind bare cobalt. Annealing in air oxidizes the exposed cobalt features. Changes in the oxidation state of these cobalt features may be studied with electron energy loss spectroscopy.

11:45 AM "H1.7"
CHEMICAL NANOLOTHOGRAPHY WITH ELECTRON BEAMS, Wolfgang Eck, Armin Gloehäuser, Wolfgang Geyer, Volker Stadler, Alexander Küster, Michael Grunze, Angewandte Physikalische Chemie, Munich, Germany.
We present new results in the generation of chemical nanostructures on aromatic self-assembled monolayers. Using electron beams, biphenylenesiloxane are cross-linked on the nanometer scale while reducible terminal groups such as nitro or cyano are locally reduced to amino functionalities. Additional molecules, such as benzene, are covalently linked to the nanomaterials so that chemically defined nanostructures with lateral dimensions below 20 nm are generated. Alternatively, the patterns can be transferred into the substrate using chemical etching techniques, such as the XPS and IR data of the chemical transformations as well as AFM profiles of the modified surfaces.

SESSION H2: PLASMON PROCESSES ON THE NANOSCALE

Chair: David P. Taylor and Thomas Orlando

Monday, December 2, 2002
Room 309 (Hynes)

1:30 PM *H2.1

SMALL IS DIFFERENT; SOME INTERESTING PROPERTIES OF MATERIAL CONFINED IN TIME AND NANOMETETER SPACE OF DIFFERENT SHAPES. Mostafa A. El-Sayed, Georgia Institute of Technology, Department of Chemistry and Biochemistry, Atlanta, GA.

The property of a material is characterized by a specific length scale for the motion of its electrons. This is determined by the forces acting on the electrons. For metals, the mean free path of the electron determines its conductivity. For semiconductor, the Bohr radius is the electron-hole separation induced by giving the semiconductor the minimum amount of energy required to separate its electron and hole, i.e., the characteristic length scale. These characteristic length scales are on the nanometer dimension. What happens if we physically reduce the size of a material to be comparable or smaller than its natural characteristic length scale? Naturally, its property will change, and equally important, becomes sensitive to its size or shape. Thus each material can, in principle, have multiple properties of new properties as we change its size or shape on the nanometer scale. In my talk, I will present our results on the change in the properties of some semiconductor and metallic nanoparticles(1) upon changing their shape. The properties studied are, the optical and radiative properties, the femtosecond electron dynamics in semiconductor nanoparticles, and the ultraviolet photothermal shape changes of gold nanorods and spheres.


2:00 PM *H2.2

TAILORING NANOPARTICLES WITH LASER LIGHT. Frank Trager, Universität Kassel, Kassel, GERMANY.

The physical and chemical properties of nanoparticles or, more generally speaking, nanomaterials, i.e., systems of reduced dimensions, depend on their size and shape and usually differ considerably from those of the corresponding bulk material of macroscopic dimensions. Therefore, assembly of such aggregates of precisely controlled size and shape on substrate surfaces or in encapsulating matrices opens the door to fabricate tailor-made materials with novel optical, structural, chemical and other functional properties. Technical exploitation of nanoparticles, however, is intimately connected to the availability of advanced techniques to produce, manipulate and characterize them in such a way that the genuine identity of each single entity is preserved while precisely controlling the dimensions. This paper gives an overview of current techniques used for the synthesis of nanomaterials of controlled dimensions and, in particular, monodisperse ensembles. Special emphasis is given to manipulation of supported nanoparticles through irradiation with continuously tunable laser light either after or during particle formation, methods that rely on excitation of surface plasmon polaritons in the particles and exploit the size and shape dependence of the resonance frequencies of this collective electron oscillation for selective manipulation [1,2]. They are applicable to a variety of metals, a wide size range and cannot only be used for narrowing of broad surface enhancement of almost monodisperse nanoparticles but even to control the particle shape independent of size. Examples of laser treatment of silver and gold nanoparticles will illustrate the enormous potential of these techniques. Finally, future developments, projects and applications will be outlined.

2:30 PM *H2.3

SUBWAVELENGTH SCALE PHOTONIC STRUCTURES. Harry A. Atwater, Stefano A. Maier, Pieter G. Kik, Andrea Martin, Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA.

The ultimate miniaturization of photonic devices towards densely integrated optical systems akin to their electronic counterparts will require structures that focus, direct, guide and switch electromagnetic (EM) energy below the diffraction limit of light. We are investigating the possibility of using structures consisting of ordered arrays of closely spaced coupled dipole oscillators, such as metal nanoparticles, for this purpose. We have developed a device/circuit theory that predicts that energy transport in these arrays occurs via resonant near-field coupling between metal nanoparticles that sets up coupled plasmon modes of the nanostructured arrays. This coupling leads to coherent propagation of energy along nanoparticle and nanorod arrays with group velocities of about 0.1c. These energies can be guided around 90 degree corners and split via tree structures with high efficiency. We have confirmed our theoretical predictions in a macroscopic analogue operating in the microwave regime via experiment, full field electromagnetic simulations and far field spectroscopy of nanostructure arrays. In order to verify the guiding properties at the nanoscale, we fabricated ordered arrays of closely spaced 30-50 nm gold and silver nanorod structures in a variety of geometries such as straight lines, corners and tree structures using electron beam lithography on ITO coated glass substrates and assembly using atomic force microscopy manipulation. We are currently working on the optical characterization of these structures using an illumination mode near field scanning optical microscope (NSOM) as a local excitation source at 14 nm close to the surface plasmon frequency of gold nanoparticles. If the guiding of electromagnetic energy at optical frequencies on the nanoscale proves to be of the same efficiency as it is in the macroscopic microwave analog, then ordered arrays of metal nanoparticles could become building blocks of nanoscale all-optical integrated circuits.

3:30 PM *H2.4

OPTICAL NANOolithography USING EVANESENT FIELDS. Richard Blaikie, Meen Akhavan, University of Canterbury, Department of Electrical and Computer Engineering, Christchurch, NEW ZEALAND.

Resolution limits for projection optical lithography are well known and well understood, but in the optical near-field region these limits can be overcome. This offers the prospect of 'optical nanolithography' without the need to use expensive, deep ultraviolet light sources [1]. We have been studying photolithography techniques that utilise exposure from evanescent fields close to metallic amplitude masks. Sub-diffraction-limited resolution has been achieved experimentally, and the theoretical resolution limits have been explored using vector electromagnetic near field simulations. Resolution down to 20nm using exposure wavelengths greater than 400nm is predicted [2]. In this talk the issues affecting the fundamental resolution photolithography close to metallic amplitude masks will be explored. It is found that the exposure wavelength is of secondary importance in this regime, and that the properties of the mask and much more significantly, the size of the features in the mask determines how well the resolution and control during mask manufacture, rather than the conventional (and costly) approach of driving the exposure wavelength deeper and deeper into the ultraviolet. Near field interference effects will also be discussed, and a proposal for spatial frequency doubling using Evanescent Interferometric Lithography (EIL) will be described [3]. Finally, the implications of this research will be presented on the use of negative refractive and surface plasmons to improve the resolution in the evanescent near field. 1. Alkaisi, et al., Appl. Phys. Lett. 76, 3560 (1995); Goodberlet, Appl. Phys. Lett. 76, 667 (2000). 2. McNab and Blaikie, Appl. Opt. 39, 20 (2000). 3. Blaikie and McNab, Appl. Opt. 40, 1692 (2001).

4:00 PM H2.5

PLASMON PRINTING – NANOSCALE PATTERN REPLICATION USING VISIBLE LIGHT. Andrea L. Martin, Pieter G. Kik, Stefano A. Maier, Harry A. Atwater, California Institute of Technology, Thomas J. Watson Laboratory of Applied Physics, Pasadena, CA.

We have recently proposed a new approach to optical lithography that could be used to print patterns with feature sizes below 60 nm using conventional photoresists [1]. This work exploits the intensity enhancement at the plasmon resonance of metal nanoparticles i.e., the collective electron oscillation (surface plasmon mode) in an optical field. Resonant excitation of metal nanoparticles strongly enhances dipole field, and a thin resist layer can be locally exposed in the resonantly enhanced near field region. Using Finite Difference Time Domain (FDTD) simulations we show that broad beam illumination produces an enhanced local intensity that varies in position depending on the incident angle of the beam. From the
FDTD simulations: the enhanced exposure area for a 40 nm Ag sphere using a p-polarized 488 nm light incident on the sample is 30-80 nm in diameter (6.05) and extends to depths of 12-45 nm in the resist. The optimum illumination wavelength coincides with the high sensitivity region of standard g-line photoresists. We also explore the importance of the medium above and below the resist layer and the angle of incidence. Printing experiments using 40 nm diameter silver colloids deposited directly onto the 55-75 nm thick g-line resist layers on PDMS and using contact lithography with masks containing 30nm diameter silver structures prepared with lift-off technique will be presented. The samples were exposed at various times using ~400nm light and subsequently developed. Atomic Force Microscopy and UV NSOM on these samples reveals nanocable depressions in exposed resist layers, providing evidence for plasmon-enhanced resist exposure. We will also present potential applications as well as some limitations of the technique. [1] P.G. Kik, S.A. Maier, and H.A. Atwater, "Plasmon Printing - a new approach to near field lithography", Nanopatterning - from nanowires to nanotubes. Integration to Biotechnology (Mater. Res. Soc. Proc., Boston 2001).

4:15 PM H2.6
THE CONSTRUCTION OF SPHERICAL ASSEMBLIES BY GOLD NANOPARTICLES MEDIATED WITH MULTI-DENTATE TETRATHIOL LIGANDS. Matthew M. Mauer, Li Han, Stephanie Lim, Chuan Jian Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY; Daniel Rabinovich, Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, NC.

The synthesis and processing of nanoparticles consisting of metallic nanocrystals were carried out by using tetra-alkylammonium halide, which provided information about the correlation of the surface plasma resonance band with the concentration and the structure of the molecular mediator. The interaction of the tetra-alkylammonium by the thiocarbonyl ligand was assessed by FTIR spectroscopic characterization. The morphological evolution from individual nanoparticles to spherical assemblies of 80 - 200 nm was determined by TEM visualization. The "soft" nature of the spherical assemblies on different substrates was determined. The results reveal an intriguing intermolecular-induced morphological change. Implications of the findings to interfacial manipulation of the nanostructures and potential applications will also be discussed.

4:30 PM H2.7
DIRECTED SELF-ASSEMBLY OF ORDERED METAL NANOCRYSTALS USING A FOCUSED ION BEAM MICROSCOPE (FIB): M.D. McMahon, A.B. Hinzel, R. Lopez, R.F. Haglund Jr., C.L. Feldman, Dept. of Physics and Astronomy, Vanderbilt University, Nashville, TN; R.H. Magruder III, Dept. of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, TN; and Dept. of Physics, Belmont University, Nashville, TN.

Metal nanocrystals are strongly confined electronic systems with a band structure drastically altered by the small size of the system and the reduced population of conduction-band electrons. Their optical response is extremely sensitive to the size, size distribution and the spatial arrangement of individual nanocrystals. Ordered arrays of metal nanoparticles have potential applications as elements of nonlinear optical devices, transistors, as sensitizers for fluorescence emitters and photodetectors, and as anchor points for arrays of biological molecules. This effort is focused on the fabrication of ordered metallic nanocrystal arrays for optical investigations. Our approach to the formation of the metal nanocrystal arrays on a spatially arranged lattice of holes prepared by focused ion beam (FIB) processing is a substrate. The holes were formed by FIB drilling in a silicon substrate with a 25 nm surface oxide. Two processes have been explored: 1) Fabrication of ordered arrays of gold nanocrystals on FIB-processed substrates using electron beam deposition; and 2) Fabrication of ordered arrays of silver nanocrystals with diameters 40-60 nm separated by 180 nm center-to-center, using pulsed-laser deposition of silver on the substrate. The metal nanocrystal arrays are characterized using AFM as well as SEM and energy dispersive x-ray (EDX) analysis. EDX analysis demonstrates that all of these clusters at sites that have been irradiated by the ion beam. These results suggest that the FIB-PLD combination can be used to create ordered arrays of Ag nanocrystals with diameters of 10 nm or less. This research has been supported by the U.S. Department of Energy under grant DE-FG02-01ER46016.

4:45 PM H2.8
NEW PROCESSING TECHNIQUES FOR THE CREATION OF MICRO-OPTO-ELECTRO-MECHANICAL MACHINES AND PHOTONIC DEVICE IMBEDDED IN GLASS. M. Abraham, Oxford University, Dept. of Materials, Oxford, UNITED KINGDOM.

Photo- writable glass is a commercially available material that can be patterned using a standard UV photon exposure and bake process. It has been developed to allow the exposure of metal ions in the glassy matrix that can form nano-crystalline nucleus sites and eventually small SiO2 or metal crystals when annealed at higher temperatures. To date the use of photo-writable glasses in the area of MEMS research has concentrated on the improvement of the exposure and etch techniques for the purpose of making small high-aspect ratio mechanical devices in this medium. This approach has been used to make gross imbedded features in the glass. We are currently developing new ways of extending the functional use of this material to the areas of MOEMS and photonics by incorporating advanced laser and ion based techniques. The immediate aim is to further reduce the scale of imbedded structures in the glass to form wave-guides of various types. The techniques being investigated include: the extension of the glass type to materials which form metal needles (as opposed to SiO2 crystals) that can be used in plasmon applications, the use of an ion beam to expose the glass and create very small imbedded nucleus sites for crystal growth, and the use of laser direct write for both the exposure and the etching of the glass. We will show the potential advantages of each of these areas of research for creating rigid waveguides in transparent medium.

SESSION H3: NANOFABRICATION VIA NONLITHOGRAPHIC TECHNIQUES

Chairs: Thomas Orlando and Koji Buto
Tuesday Morning, December 3, 2002 Room 309 (Hynes)

8:30 AM H3.1
SHAPE VARIATIONS AND CONTROL IN SELF-ASSEMBLED METAL NANOCLUSTERS. Rina Tennebaum, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

The use of polymers as stabilizing agents for the controlled synthesis of metal nanoclusters can be extended also to the manipulation of cluster shape. The preferential adhesion of polymers to distinct crystallographic faces of the growing metallic fragments, causes a distortion of the cluster shape, since the growth directions become differently hindered by the polymer. The result is a high degree of anisotropy in the cluster shape. Various iron-polymer systems are studied in order to determine the precise parameters which govern such preferential adsorption. Systems in which the same polymer has been used but the reaction conditions were different, exhibit different particular shape. For example, in the presence of poly(vinylidene difluoride) (PVDF), the thermal treatment of a metal precursor-polymer solution that is annealed and polymer film formation ('hot' method), gives rise to nanoparadoms. On the other hand, the thermal treatment of a metal precursor-polymer solution that is performed after solvent evaporation at room temperature (cold method), gives rise to nanospheres. In the former case, the solvent is present in the initial stages of the reaction, allowing a higher degree of mobility of the growing nanoclusters and the polymer chains, while in the latter case, the metal precursors are immobilized in the polymer film. Additional examples include the formation of Fe nanorods in the presence of poly(methyl methacrylate) (PMMA), and the formation of nanostrians in the presence of poly(carbonate) (PC). As an important step in understanding the underlying molecular mechanisms responsible for the shape selectivity of metal nanoparticles in the presence of various polymers, we will attempt to relate the particle shape variation to the strength of the metal-polymer interaction and the effectiveness of the capping process by the adsorbed polymer layer.

9:00 AM H3.2
SELF-ASSEMBLED HIERARCHICAL-STRUCTURES OF EMULSIONS AND FINE PARTICLES. Sachiko I. Matsuihita, RIKEN Frontier Research System Project, RIKEN Hierarchy Structures Lab, Saitama, JAPAN; Nobuhito Kuroko, Masasatoyu Shinomura, Hokkaido Univ, Research Institute for Electronic Science, Hokkaido, JAPAN.

Various production methods such as conventional lithography, soft lithography, self-assembly, are used to obtain nanoscale to micromolecular architectures, which are considered extremely important from the
point of view as photonic crystals, electron emitters, high-density optical storage media, catalytic systems, and so on. Among them, since Friggio wrote the novel print in 1977, dissipative process is well known that it is potentially of great scientific and technological interest because the process is simple, self-assembly, inexpensive system to prepare wide-range structure of micromorphic. Especially, one of the important points of dissipative process is capability to make hierarchy structures that will bring diversity and complexity, as everything does. Among many dynamic processes such as dissipative structures, we attracted honeycomb-like structures. This honeycomb-like structure can be formed in a vapor phase deposition layer of polymer suspensions by the evaporation in humid air, and the final structure has hexagonal hole-packed surfaces (0.2-10 µm diameter) like a comb of honeybees. Possible applications of such honeycomb structures include membranes for separation, microreactors, biointerfaces, catalysts, and microstructured electrode surfaces, however, in this presentation, a new application as a self-assembly system to prepare hierarchical structures will be reported. Honeycomb (A U, Cu) in various gases like water/steam vapors or liquid solutions can be formed. Production of honeycomb structures is achieved by using a novel technique of vapor phase deposition. The deposition process is a two-step process: (1) Deposition of a thin film of Xe on the surface, (2) Evaporation of the deposited layer. The resulting structures have a high degree of order and can be used as optical elements in various applications.

9:30 AM #3.4
THE FORMATION, CHARACTERIZATION, AND INTEGRATION OF NANOSTRUCTURES: Ag AND Si. John H. Weaver, University of Illinois, Department of Materials Science and Engineering, Urbana, IL.

In the area of nanostructures, the goal is to produce structures of arbitrary material on a substrate of arbitrary material, with size selection and patterning so that new science can be learned and new devices can be fabricated. There are many ways to approach this synthesis, and all have their limitations. In our laboratory, we have developed techniques for the production of nanostructures of a wide range of materials and to deliver them to atomically clean surfaces (of any type) where their interactions can be investigated. The process involves the thermal evaporation of Xe which nucleation and growth occurs at 50 K. Subsequent desorption of the Xe delivers the clusters in the ultimate of soft landing. This technique allows us to control the size and shape of the Ag dots as well as the deposition rate, and we are currently investigating the use of this technique for the production of nanostructures.

10:30 AM #3.5
WIND-DRIVEN WAVES AT A MOLECULAR SEASHORE. C. Mathew Mate, IBM Almaden Research Center, San Jose, CA.

We have all noticed the intricate wave patterns that wind generates on the surfaces of lakes and oceans. On these macroscopic liquid surfaces, the driving force for wave formation is wind shear, while the forces of gravity, surface tension, and viscosity work to smooth these surfaces. In this talk, I'll show how wind shear can generate and manipulate wave patterns on the surfaces of molecularly thin liquid films. For these ultra-thin films, molecular forces dominate over the forces of gravity and surface tension. This results in a new class of wave patterns, which are highly sensitive to the presence of underlying substrates and the liquid molecules in the flow. I'll discuss the implications of these results for lithography of nanometer thick films and the potential for using wind-driven waves for nanostructure formation.

11:00 AM #3.6
RESOLUTION, FIDELITY, AND REGISTRATION OF DIRECTLY PRINTED PATTERNS OF MICROELECTRONIC MATERIALS. Sigurd Wagner, Scott M. Miller, Anton A. Darhuber, Samir Saccor, and Sandra M. Tress, Dept. of Electrical and of Chemical Engineering, Princeton University, Princeton, NJ.

The direct printing of patterned active electronic materials has been attracting considerable interest recently, because it could reduce the cost of electronic circuits and MEMS well below that of the conventional deposition, modification and patterning of device layers. This cost reduction may derive from the reduction of process steps, massively parallel printing of large areas, or roll-to-roll manufacturing. At present the dominant applications of direct printing are making printed-wire boards, where passive components like capacitors are printed in addition to interconnects. It is likely that direct printing will extend up to larger and more complex device layers, such as micro and nanostructures, and even cover the entire range of scale in the form of large area electronics. Printing of device layers is a potential application of direct printing for the fabrication of micro and nanostructures. Overlay registration becomes important when complete devices must be printed. A large range of printing techniques is available; it covers impact and non-impact printing, with impact printing including additive and displacement techniques. To date few inks and processes have been developed specifically for the printing of active electronics. Therefore, techniques that are being dominated by the inks that are available rather than by the devices that are desired. This situation explains the preponderance of printed etch masks instead of device layers, which are not yet realizable. The main reason is the need for precise alignment. The principal issues associated with any printing technique are the resolution of the printed device layer and the fidelity of the printed pattern to the desired design. No new technique has been demonstrated for overlay alignment. We will categorize the issues associated with the direct printing of electronic devices, and focus our discussion on pattern production and pattern fidelity.

11:30 AM #3.7

The realization of a polymeric injection laser diode is an important aim in organic electronics. A step towards this goal lies in the understanding and fabrication of feedback structures for lasers. Such feedback structures may either be fabricated in the substrate or directly in the active polymer layer. Soft Lithography has proven itself as a useful tool to pattern a wide variety of materials. Typically one uses elastomeric molds (stamps) to pattern materials and structures with dimensions as low as 30 nm can be achieved. We present a direct imprinting process based on soft lithography to fabricate a laser feedback structure directly on a liquid-crystalline type active electroluminescent polymer. The utilized polymer allows for a low
temperature imprinting process due to its low glass transition temperature. We will report on the application of this approach to produce optical feedback structures for optically pumped laser arrays.

11:45 AM H3.8
NANOSCALE SCIENCE & TECHNOLOGY – A GATEWAY TO NEW PRODUCTS, PROCESSES AND PROPERTIES IN THE CHEMICAL INDUSTRY. Raymond Oliver, David Sutton, Derek Graham, ICI Strategic Technology Group, Redcar, UNITED KINGDOM.

The Chemical and Process Industries (CPI) has witnessed massive changes over the last decade. Much of the Oil and Petrochemicals industry production has shifted irreversibly to the Middle and Far East and has been replaced by biochemical and specialty materials market opportunities. Waiting in the wings is the huge potential offered by “small technology” concerning nanoscopic and nanostructured materials generation. In this talk I will try to give a view of some of these opportunities from the point of view of a specialty materials and consumer products business and in particular how Chemical Engineering Principles still apply even although the process/product technologies are closer to those developed for semiconductor and electro ceramics industry sectors. It is also a fact that most fine materials and structured materials in the chemical industry are synthesized and assembled in the same way that a simple single component system may or may be complex consisting of two or more phases in the presence of surface active molecules for example. The ability to process such materials without losing valuable structure and organisation within the material is a key element of providing useful Nanoscopic materials. The trend over the next few years will be to move towards Molecular Manufacturing principles through scale-down, replication and so called “bottom-up” product synthesis and assembly with an increasing emphasis on effect and functionality while still retaining efficiency and availability. In this context “granular materials” has to be viewed in hierarchical terms, where the relevant length scale may move from approximately 100 microns for bulk storage and flow to microns for redispersible aggregated primary particles to 1-10 nm for “quantum dot” type nanochusters which exhibit spectacular changes in luminescence for example. I will illustrate the above with examples of nanoscopic synthesis and assembly processing technologies which deliver extreme effects and functionality.

SESSION H4: FABRICATION AND PROPERTIES OF 2-D ORDERED NANOSTRUCTURES
Chair: Rolf Bolma and Linda Masoj
Tuesday Afternoon, December 3, 2002
Room 309 (Hynes)

1:30 PM H3.1
TWO-DIMENSIONAL ORDERED NANO PORE ARRAYS:
FABRICATION AND FILLING WITH MATERIALS. Ulrich Gossele, Konstanz Schub, Frank Mueller, Sven Matthias, Manfred Reiche, Ralf Wemhöhn, Josseb Choi, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

We have investigated two-dimensional ordered pore arrays and their filling with materials such as various metals or based on two different material systems. One material system involves pores in silicon, the other one pore arrays in aluminum oxide fabricated by anodic oxidation of silicon. In the case of silicon, the location of the pores has to be predefined lithographically. The pore diameter can be varied during the etching process. Subsequent filling with a metal leads to a metal mesh with varying diameter. The diameter variation may be used to encode information in an optically readable way. In the case of anodic oxidation the ordering of the pores is based on a self-limited process which does not allow long range order. Long range order may be obtained by a combination of nano-imprint and self-ordering.

Filling of the pores with ferromagnetic materials allows to fabricate ordered ensembles of ferromagnetic nano-wires which might be of interest for future high-density magnetic storage concepts. Further examples of filling of pore arrays will be given.

2:00 PM H4.2
3-D NANOSTRUCTURE FABRICATION BY NANOIMPRINT LITHOGRAPHY & LITHOGRAPHICALLY INDUCED SELF-ASSEMBLY Paro Deshpande, Zhaoning Yu, Wei Wu, Mingtao Li, Bo Cui, Xinya Lei and Stephen Y. Chou, NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, NJ.

As semiconductor devices continue to shrink, low-cost, large area, 3D nano-patterning is becoming increasingly significant. Such 3D nano-patterning is also needed in areas such as nano-optics, nanobiology and MEMS/NEMS just to name a few. In this talk, we present two innovative approaches to large area nanofabrication that can be extended to three-dimensional structures. The first, nanoimprint lithography (NIL), is a low cost, high throughput nano-patterning process in which a mold is used to photolithographically deform a polymer resist (1). Sub-10 nm feature sizes and uniformity over large areas have both been demonstrated. Using a 3D mold, 3D patterns can also be created. The second is lithographically induced self-assembly (LISA), a process in which a mask held above a thin polymer film is used to induce periodic pillar arrays in the polymer (2). The pillars bridge the gap to nanowires.

Furthermore, the pillars can be aligned to patterns in the mask allowing for precise control of the position and crystal structure of the pillar arrays. Such structures can be used as templates for 3D architectures or as features on top of pre-existing patterns.


2:30 PM H4.3
OPTOELECTRONIC NANOSTRUCTURES. Gennaro S. Pomeze, Air Force Office of Scientific Research, Arlington, VA.

Nanotechnology and nanoengineering as applied to optoelectronics offer opportunities and challenges for new generation devices. The convergence of nanotechnology, material processing, tools, and applications is driving the realization of integrated photonics and the all photonics chip. Part of this approach is photonic crystals. Building these crystals requires creating periodic structures from dielectric materials that repeat themselves exactly and at regular intervals. If the matrix is made precisely the resulting structure may have a photonic bandgap, a range of forbidden frequencies within which a particular wavelength may be blocked, and the electromagnetic radiation is reflected. Photonic bandgap structures and the associated nanofabrication allows photonics to advance optoelectronic miniaturization, light localization, and highly integrated optical devices and components. Lithographic techniques like focused ion beam, e-beam or extreme UV lithography play part in this miniaturization. However, these techniques have their limitations in terms of materials that can be patterned and the associated capital investment is high. Alternative techniques are needed based on self-assembly of inorganic and organic particles into regular nanostructures, soft lithography, nanopores, and protein and biological scaffolds. Example alternatives could be block copolymers that can be designed to mimic biological membranes, and distones with their intricately patterned wall that consists of amorphous silica. Understanding the molecular mechanisms that control these alternative types of nanofabrication will be a challenge.

3:30 PM H4.4
SELF-ASSEMBLY OF NANOSHEETS USING MAGNETIC FIELD. Jean-Christophe P. Gabriel*, Frank Camerel, Patrick Batail, Sciences Moleculaires aux Interfaces, CNRS, Nantes, FRANCE, Bruno J. Lemaire, Patrick Davidson, Lab Physique des Solides, CNRS, Orsay Univ, FRANCE, Hervé Desvouzys, Service de Chimie Moléculaire, CEA, Saclay, Gif-sur-Yvette, FRANCE; Present address: Nanomix Inc., Emerville, CA.

We will present the first example of a lamellar phase comprised of inorganic solid-like nanosheets (i.e. in which all atoms involved in the sheet are covalently bonded) dispersed in water. The spacing between these nanosheet can be tuned from 1.5 to 6 nm by oriented bulk samples can be obtained by mechanical or magnetic alignment. This property was used to measure residual dipolar couplings for the structure determination of biomolecules by liquid-state NMR.

3:45 PM H4.5
GELATION OF A SYNTHETIC, β-SHEET-DERIVED PEPTIDE. Nathan Lockwood, Univ of Minnesota, Dept of Chemical Engineering and Materials Science; Robert van Tilbeurgen, Univ of Minnesota, Dept of Biotechnology, Minneapolis, MN.

We observed gelation of a 23-residue peptide derived from the β-sheet domain of platelet factor-4 (PF4sf-46). Optical and electron microscopy revealed gels composed of heterogeneous mixtures of 50 to 200 μm spherical aggregates in a less-dense gel matrix. Infrared and circular dichroism spec troscopies showed that gelation involved the conversion of PF4sf-46 from an unstructured, random coil state to an extended β-sheet conformation. In the extended β-sheet conformation, we used aggregation-induced NMR peak intensity decay to show that temperature, pH, and ionic strength influenced PF4sf-46 gelation rates. Under identical solution conditions, gel formation took days at T < 50°C, but only 30 minutes at T > 50°C. Gelation was most rapid at pH values near the pKa of His(s), the central residue of the peptide. Increases in solution ionic strength reduced the critical gelation concentration of PF4sf-46. The results of our study share characteristics of self-assembling peptides reported by other groups. Based on our results, we pose a hypothetical
model of PF24-gelation in which the development of parallel or antiparallel β-sheet character leads to extensive self-assembly via intermolecular hydrogen bonding, followed by hydrophobic associations of the resultant β-sheets into extended networks. Intermolecular electrostatic repulsions between peptide sidechains and N-termini moderate the rate and extent of self-assembly.

4:00 PM H4.6
SYNTHESIS AND CHARACTERIZATION OF METAL NANO-PARTICLES IN AMORPHOUS CARBON FILMS. I. Gerhardt, H. Hofstätter, and C. Ronning, II. Physikalisches Institut; H. Gibhardt, Institut für Physikalische Chemie; M. Seite, IV. Physikalisches Institut, Universität Göttingen, Göttingen, GERMANY.

Metallic particles in the size of a few nanometers embedded in a dielectric matrix material offer a wide range of qualities, as for example nonlinear optical behavior, enhanced field emission properties, and the potential to be used in a variety of electronic media. This motivated our study on the formation of metal nano-particles in diamond-like amorphous carbon (a-C). The structural properties of metal containing amorphous carbon thin films (a-C:M, M = C, Ag, Au, and Fe) synthesized by mass selected ion beam deposition (MSIBD) have been characterized using X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), reflection electron energy loss spectroscopy (REELS), and magnetic force microscopy (MFM). The films were grown from highly pure metal targets at constant ion to carbon ion ratios at room temperature on silicon substrates by co-deposition of low energy carbon and metal ions. The carbon matrix proves to be diamagnetic with a high spin-band covering at low metal concentrations and becomes more graphite like with increasing metal content. Copper forms nano-particles within the matrix due to the vanishing solubility in carbon. The sizes of the embedded Cu clusters are in the order of nanometers and vary with the Cu concentration. These and other dependencies will be presented together with model assumptions on the formation mechanism of the clusters upon ion beam impact.

4:15 PM H4.7
A BOTTOM-UP APPROACH TO POLYMER/CARBON NANOTUBE FILMS. Jason H. Rouset,1, Peter T. Lelleher,2 Emilie J. Stiehl3, ICASE4, Advanced Materials and Processing Branch5, NASA Langley Research Center, Hampton, VA.

The use of molecular interactions to assemble polymer/single walled carbon nanotube (SWNT) films with high degree of order is being discussed. Using carbon nanotubes dispersed in an amorphous carbon matrix, films with high degree of ordering can be achieved. These films exhibit unique electrical, mechanical, and thermal properties.

4:30 PM H4.8
SELF-ORGANIZED ZnO NANOISLANDS WITH LOW-DIMENSIONAL CHARACTERISTICS ON SiO2/Si SUBSTRATES BY METALORGANIC CHEMICAL VAPOR DEPOSITION. Sang-Woo Kim, Shigeo Fujita, Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN; Shizuo Fujita, Kyoto Univ, International Innovation Center, Kyoto, JAPAN.

ZnO is a semiconducting material with a wide band gap of 3.3 eV at room temperature. Due to its remarkable excitonic properties based on the large exciton binding energy (60 meV), significant effects promising for achieving large oscillator strength, nonlinear optical properties, or multielectron interaction may be expected in low-dimensional ZnO nanostructures. In this paper, we report the successful growth of ZnO nanoislands with low-dimensional characteristics, which may lead to the enhanced exciton confinement, on SiO2/Si substrates by metalorganic chemical vapor deposition by introducing either N2O or O2 gas as an oxygen source and diethylzinc as a silicon source on thermally grown SiO2 layers on Si (111) as a function of the growth time, the substrate temperature, and the source flow rate. Investigation by atomic force microscopy showed that the density and size of the ZnO islands were changed by the growth condition. Reactive NO gas, which had an oxygen source was found to be a key in order to obtain uniform ZnO nanoislands with narrower size distribution and higher density. At the present stage, the height distribution was varied from 3 to 5 nm and the density in the order of 1016 cm⁻² could be obtained. More recent study is effectively going on to decrease the size and increase the density. In macroscopic photoluminescence measurements at 10 K using a 355 nm Nd:YAG laser, we observed the broad peak with a band tail up to about 3.55 eV located at the higher energy with respect to band edge emission of bulk ZnO with the free exciton emission located at about 3.38 eV. This result indicates that these ZnO nanoislands have low-dimensional quantum effect characteristics. Detailed optical characterizations are still in progress.

SESSION H5: FABRICATION AND PROPERTIES OF NANO WIRES, NANORODS AND NANO TUBES
Chairs: Koji Iwata and Thomas Orlando
Wednesday Morning, December 4, 2002
Room 309 (Hynes)

9:30 AM H5.1
SELF-ASSEMBLY OF MULTIDIMENSIONAL NANOROD STRUCTURES ON SURFACES. Sarah K. St. Angelo, Benjamin R. Martin, Thomas J. Larrabee, Thomas E. Mallouk, The Pennsylvania State University, Department of Chemistry, State College, PA.

We have studied a variety of surface-rod and rod-rod interactions using electrochemically grown nanorods (80-200 nm in diameter and 1-6 microns in length). These studies have provided us with strategies to attune two-dimensional and three-dimensional assemblies of nanorods. Typically, materials are derivatized with a SAM of forming molecules to define their surface chemistry and control their interactions. We have found that controlling the dimensions of the rods and their surface chemistry result in the formation of ordered phases resembling nematic and smectic liquid crystalline phases. Rod-like structures may be obtained by employing lithographically patterned substrates. Micron contact printing has been used to pattern surfaces with a variety of SAM forming molecules whose domains are commensurate with the substrate. This spatially resolved surface chemistry allows us to assemble structures on relatively flat surfaces. We have developed a color-coding technique that aids in the visualization of structures as they are forming and provides us with a simple means to quantify surface diffusion and phase behavior of rods in these systems.

9:00 AM H5.2
NANOWIRES AND NANO SPRINGS: UNEXPECTED CATALYST MEDIATED GROWTH PHENOMENA. David N. McElroy, D. Zhang, A. Alikhateeb, H. Han, University of Idaho, Dept. of Physics, Moscow, ID; M. Grant Norton, Washington State University, School of Mech. and Mat. Eng., Pullman, WA.

The role of the metallic catalyst in the synthesis process of microwhiskers and nanowires has been well understood since the mid-1960s. Specifically, the metallic catalyst, when in the metallic state, facilitates the absorption of material from the vapor phase. In turn, the absorbed material is transported through the catalysts to a solid interface where it is used to build the ensuing nanowire. This mechanism is known as the Vapor-Liquid-Solid (VLS) mechanism of filament growth. Only recently has the effects of the catalyst dynamics on nanowire geometry been realized. Under the appropriate conditions helical growth of nanowires, or nano springs, can be
achieved. The prerequisites for nanowire formation are as follows: (1) The composition of the nanowire forming the nanowire must be amorphous or semi-crystalline. (2) The catalyst must have a spherical geometry. (3) the catalyst diameter must exceed that of the nanowire forming the nanowire. To date, boron carbide nanowires have been realized, however, nanowire formation can be developed indicates that it is possible to synthesis nanowires from a wide variety of semiconductor and ceramic materials. The catalyst must be used in controlled amounts to determine the composition of the nanowires or nanowires. Specifically, by achieving the appropriate balance between precursor partial pressure, total pressure, substrate material and the solubility of elements within the catalyst, the elemental composition of the nanowires can be controlled. A detailed discussion on the feasibility of nanowire heterostructures based on composition modulation will be presented.

9:30 AM *H6.3* CARBON NANOTUBE-CONDUCTING POLYMER NANOCOMPOSITES: STRUCTURE AND ELECTROCHEMICAL PROPERTIES. Mark Hughes, George Z. Chen, Milo S.P. Shaffer, Derek J. Fray, Alan H. Windle, University of Cambridge, Depatr of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

The electrochemical growth of carbon nanotube-conducting polymer composites offers the ability to produce three-dimensional nanostructured materials that combine the redox charge storage mechanism of conducting polymers with the high surface area and conductance. This desirable merging of properties presents new opportunities to produce superior materials for applications such as supercapacitors, sensors and actuators. The work described here relates to electrochemically grown composite films of multiwalled carbon nanotubes and conducting polymers such as polypyrrole and poly(3-methylthiophene). By manipulating such factors as the alignment, concentration, surface treatment, type and dispersion of nanotubes in these composite, it was found that the nanocomposite structure and its electrochemical behavior could be closely controlled and customized. Interestingly, when negatively charged functional groups were attached to the nanotube surface using an acid-treatment process, the nanotubes were able to meet the dopant requirements of the conducting polymer during film growth, allowing excellent interaction between the nanotubes and conducting polymer. Using the factors described above, it was possible to minimize ionic diffusion distances within the nanocomposite films, in addition to reducing their electrical and ionic resistance. Consequently, electrochemical capacitance in excess of 2 F/cm² were obtained for the composite films with rates of response that were more than an order of magnitude higher than those of similarly prepared pure conducting polymer films. These exceptionally high values of capacitance (more than double that of either component material) and rates of response illustrate the bulk property benefits to be gained from combining carbon nanotubes and conducting polymers on the nanoscale.


Due to quantum confinement effects, nanotube-based nanomaterials are expected to show distinctive optical and electronic properties from bulk materials. A number of novel nanocrystalline structures, such as carbon nanotubes and semiconductor nanowires, have been fabricated and studied, because of their potential for a wide range of applications. The controlled growth of the nanotubes was achieved by using a focused ion beam (FIB) assisted localization of catalyst, with subsequent decomposition of hydrocarbon gas (C2H2) in a chemical vapor deposition reactor. The Cds nanowires were synthesized using the thermal evaporation of Cds powder with the presence of Au catalyst. This growth is controlled by the conventional vapor- solid-liquid (VLS) mechanism. The diameter, length, and growth directions of the nanotubes and nanowires were modified by varying different preparation parameters. The electron field emission of the nanotubes and nanowires was studied using a field emission microscope (with a base pressure ≈1x 10⁻⁶ Torr) equipped with a Faraday cup and a spectrometer. The measurement suggests that low bias voltage towards the zero bias was used to characterize the carbon nanotubes. The current fluctuations observed in the Faraday cup current. Power spectral densities with regions following various (1/f)” characteristics were observed in the current fluctuations. During electron emission measurement, the field induced light emission of carbon nanotubes was observed as the applied voltage increased from 300 V to 700 V. The electron and light emission mechanisms of nanotubes and Cds nanowires will be discussed.

10:30 AM *H6.5* GRAPHITE-BASED ELECTRONICS. Claire Berger, Yan Yi, and Wold A. de Heer, School of Physics, Georgia Institute of Technology, Atlanta, GA.

Carbon nanotubes are currently actively investigated for their electronic applications potentials. We have recently found that carbon nanotubes are ballistic conductors at room temperature with mean free paths exceeding 50 nm. Nanotubes found to be conducting nanotubes or metals depending on their geometry and doping and innovative transistor prototypes have been demonstrated. These advances show that nanotubes may indeed have applied electrical potential. On the other hand, it is not well known that the impressive electronic properties of nanotubes are common to other graphitic structures as well. We will present possible schemes for the interpretation of experiments, which function as active circuits. We also present recent attempts to lithographic pattern graphite in order to realize active nanographic devices.

11:00 AM *H6.6* GRAPHITE NANOSONES: NEW FAMILIES OF CARBON NANOSONES. Victor R. Coluci, Schelis P. Braga, Sergio B. Legoss, Douglas S. Galvao, Applied Physics Department, State University of Campinas, SP, BRAZIL, Ray H. Baughman, Nanotech Institute and Department of Chemistry, University of Texas at Dallas, TX.

Carbon nanotubes have been object of great experimental and theoretical interest as evidenced by great amount of work carried out in the last years. Although nanotubes containing heteroatoms (N, B, etc.) have also been studied, new forms of carbon-based materials could represent a potential alternative for conventional carbon nanotubes (CNTs). One example of these forms is the graphene, an allotrope of carbon consisting of planar molecular sheets containing only sp² carbons in the form of aromatic six-membered rings that are interconnected with acetylene groups. In this work we propose new families of carbon nanotubes based on graphene motifs. In analogy with CNTs, these graphene nanotubes would enable unprecedented shell doping, as well as rapid materials transport through the nanotubes sidewalls. Chemical stability and possible routes for synthesis are also addressed.

11:15 AM *H5.7* FIELD EMISSION PROPERTIES OF BN/C AND BNGC NANOTUBES. Vincent Meunier, Thomas Zacharias, Oak Ridge National Laboratory, Oak Ridge, TN, Christopher Roland, Jean Bernholc, North Carolina State University, Raleigh, NC, Marco Buongiorno Nardelli, North Carolina State University, Raleigh, NC and Oak Ridge National Laboratory, Oak Ridge, TN.

The discovery of carbon (C) nanotubes as a material with outstanding mechanical and electrical properties has led to a quest for other novel graphene-based structures with technologically desirable properties; the closely related boron (B) nanotubes (N) and mixed BNC nanotubes and nanowires have electronic properties that are complementary to pure carbon nanotubes. The polarized BN bond gives rise to important effects in the electronic properties of BN-doped carbon nanotubes. In particular, BN nanotubes possess a non-zero spontaneous polarization that makes them strong pyro- and piezoelectrics. BN/C hybrids can exist in two distinct configurations: a quasi-1D BN/C heterostructure or a quasi-2D multi-walled tube with separate BN and C shells. In the former, the BN and C phases are covalently joined while they are segregated in the latter. In this talk, we show that the introduction of BN sections into carbon nanotubes leads to a large increase in the field emission properties at the carbon tip. This is due to the intrinsic electric field associated with the BN polar network, which induces a substantial reduction in the work function at the carbon tip. The change in the work function greatly improves the field emission properties, since the decrease in the work function exponentially increases the current density. Using state-of-the-art ab initio calculations, we show that this effect is present in both BN/C and BN/C systems. While the improvement is limited in the coaxial geometry, the current density is predicted to increase by up to two orders of magnitude in the BN/C systems.

11:30 AM *H6.8* METAL NANOWIRES ARRAYS FOR CHEMICAL SENSING.
Phophotophysical effects and high probability for influencing target interaction processes. The properties of these photophysical groups are examined in the form of thin films, the rheology of photo-sensitive particles, and as colloidal crystal self-assembled photonic band gap structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

2:15 PM H6.3 ATTACHMENT OF GOLD NANOPEARL TO CARBON NANOCTUBES BY CHEMICAL MANIPULATION: Kiyang Zhang, Ann Bissen, Linda S. Schader, Pulickel M. Ajayan, Mauricio Terrones*, Richard W. Siegel, Rensselaer Polytechnic Institute, Troy, NY; *Fullerene Science Center, CPES, University of Sussex, Brighton, UNITED KINGDOM.

Since their discovery in 1991, carbon nanotubes have been of great interest because of their unique structural, electrical and mechanical properties. Their potential applications include nanodevices, quantum wires, ultrahigh-strength engineering fibers, sensors, catalyst supports, etc. Moreover, carbon nanotube-based materials make it possible to fabricate some intriguing nanostructures. In this study, we present the sensitive gold nanoparticles to carbon nanotubes by chemical modification of the carboxyl groups in the nanotubes. The TEM studies showed that well-dispersed gold nanoparticles decorate the walls and ends of the nanotubes. This result indicates that functional Au nanoparticles on carbon nanotubes via chemical modification are present not only on the ends, but also along the length of the nanotubes. The approach used is simple and versatile, and can be used to attach many other nanoparticles (e.g., semiconductor nanocrystals, magnetic nanoparticles, etc.) to the carbon nanotubes.


Monolayer-protected nanocrystals possess unique optoelectronic properties which can be tuned by adjusting the cluster composition, dimensions and capping layer chemistry. Interlinking these nanocrystals using molecular connecting agents and 2D assemblies is of interest for harnessing these properties in creating larger-scale, more complex devices. Here, we describe phase transitions in 3D assemblies of octanethiol (OT)-capped nanocrystals of Ag and CdS of sizes ranging from 2 to 10 nm. We use a combination of differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and infra-red spectroscopy (IR) to study microcrystal analysis (TGA) and in situ polarized microscopy (PLM) of our studies. DSC measurements reveal two melting-type reverse transitions at ~47 and 129°C in assemblies of OT-capped Ag nanocrystals, which are solids at room temperature. TEM of the assemblies show interlinked nanocrystals in a close-packed configuration, due to hydrophobic interactions between the OT caps. Neither the nanocrystals nor the assemblies show observable structural changes after thermal cycling, indicating that the phase transitions are due to OT. PLM measurements of the first transition correspond to the melting of a phase comprised of excess OT i.e., those not attached to the nanocrystals. The second transition corresponds to the "melting" of the nanocrystal assembly due to increased mobility of the OT molecules that cap and interact with alkyl chains attached to adjacent nanocrystals. Heating above 150°C leads to the disappearance of the phase transitions during subsequent cooling and heating, indicating desorption and breakdown of OT caps. Unlike Ag-OT, Au-OT and CdS assemblies are liquids at room temperature. Au-OT shows only one reverse transition near 0°C, corresponding to the second transition described above, while CdS-OT shows no observable transitions between 20 and 250°C. We explain these results in terms of the strength of interactions between OT and the nanocrystals.

2:45 PM H6.5 CRITICAL UNIVERALITY AND MAGNETIC PHASE TRANSITIONS OF A MODEL NANOCRYSTALLINE FERROMAGNET: A MONTE CARLO STUDY: Guang-Ping Zheng and Mo Li, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

The critical scaling properties of a model ising model is investigated using Monte Carlo simulations in the digital sample of an ensemble of nanocrystals. The effects of the microstructural properties (grain size, grain size, distributions and grain boundaries are modeled using a new algorithm. Using the cluster algorithm, we calculated the
magnetization and magnetic properties of the model nanocrystalline sample. It is found that despite the shift of the critical temperature, all the critical exponents of being model remains the same as those in the pure system. The nanocrystalline being system, therefore, remains in the same universality class.

3:30 PM H6.6
SUPERCONFORMAL FILM GROWTH IN SUBMICRON FEATURES. T.P. Moffat, D. Wheeler, B. Baker, and D. Josell, NIST, Gaithersburg, MD.

Electrodeposition of copper has been implemented in the fabrication of the latest generation of integrated circuits resulting in faster clock speeds, enhanced reliability and lower processing cost. Central to the success of the process is the ability to yield void and seam-free, bottom-up filling of high aspect ratio trenches and vias. Early models of "superfilling" assumed location-dependent growth rates derived from diffusion-limited accumulation of an inhibiting species. Such models were unable to predict several key experimental observations. Recently, a curved enhanced accelerator coverage (CEAC) mechanism has been used to quantitatively predict superconformal electrodeposition of copper and silver in trenches and vias. The model provides a simple explanation for the long-standing observation of the smoothing action provided by certain electrolyte additives (traditionally referred to as "brighteners"). The construct has also been extended to quantitatively explain superconformal chemical vapor deposition (CVD).

3:45 PM H6.7
MODELING THE FLOW OF BINARY FLUIDS IN A PATTERNED MICROCHANNEL. Olga Kubenok, Anna Blago, Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA; David Jasnow, Physics Department, University of Pittsburgh, Pittsburgh, PA; Julia Yoon, Theoretical Physics Department, Oxford University, Oxford, UNITED KINGDOM.

We develop a three-dimensional hydrodynamic model that reveals the thermodynamic behavior and flow patterns of a binary fluid moving over patterned substrates within a microchannel. The binary fluid consists of two immiscible components, A and B, that are subjected to a Poiseuille flow. We model patterned substrates by introducing domains with preferential wetting interactions for the A or B components. We investigate how the patterned substrate can be exploited to create additional interfaces between the A and B components and to yield relatively wide regions of mixed fluids inside the microchannel. We also isolate conditions that drive the periodic formation of a droplet on the neutral wall and the movement of the droplet along the channel. The droplet size and velocity strongly depend on the interfacial tension between the A and B fluids and the interaction with the patterned substrate. The results provide guidelines for controlling the fluid flow and for creating localized "mixing stations" within microfluidic devices.

4:00 PM H6.8
FINITE ELEMENT ANALYSIS OF NANOSCALE THERMAL MEASUREMENTS OF SUPERLATTICES. Jason R. Foley and C. Thomas Avedissian, Thermal Sciences Laboratory, Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY.

Thermal wave techniques are widely used for characterizing the thermal properties of bulk materials and thin films. In the data analysis of these experiments, the samples are assumed to be either solids or infinite planar films, resulting in one- or two-dimensional heat flow. However, only certain samples geometries and experimental conditions satisfy these assumptions and, if violated, can lead to significant errors in the thermal property estimates, e.g., edge effects in micro- or nanoscale mesa or patterns. We present, for the first time, a finite element analysis for two- and three-dimensional heat flow in samples of arbitrary shape and composition. The finite element formulation is summarized and the governing differential equations for the heat transport are reviewed. Various boundary conditions are considered, including thermal boundary resistances at interfaces, applied heat fluxes, and insulated surfaces. Experimental data from bulk and nanofabricated materials systems are presented and analyzed, with special attention to measurements of superlattices.

4:15 PM H6.9
PROCESSING IN MATERIALS THAT MEDIATE THREE-DIMENSIONAL FABRICATION. H. Helvajian, Laboratory Operations, The Aerospace Corporation, Los Angeles, CA.

As feature size is reduced the material/compound that comprises the "building-block" unit must, with increasing relevance, participate in the assembly process. This is especially true in three-dimensional fabrication and for feature sizes accorded in nanofabrication.

Therefore, "reagent" materials or substrates that can be tailored to mediate in the material processing and fabrication will be more of a necessity. For fabricating features in the microns realm and for structures/devices that must be in glass or ceramic material, we have found a material that has this mediating effect. The material is a photostructurable glass ceramic, skin to ceramic kitchenware and for processed much like that in photography. A laser with a wavelength that is tuned to material excitation is used to impregnate a 3D volume image in the glass substrate by a direct-write photolithography. The stored image can then be selectively etched in hydrofluoric acid. We have fabricated true 3D structures that have numerous applications in MEMS, microfluidics and nanowire electronics. These structures cannot easily be fabricated without resorting to countless masking steps. The current technique has size resolution down the micron level, but has the potential to go smaller. We will present the developed 3D material fabrication process, structures and devices fabricated in the microns feature size resolution realm and the approaches being taken to go lower.

4:45 PM H6.10
EVOLUTION OF CARBON SELF-ASSEMBLY IN COLLOIDAL PHASE DIAGRAM. Vaclav Bouda, Czech Tech Univ, Dept Mechanics and Materials Science, Prague, CZECH REP.

The growth of the self-assembled structure of carbon colloidal particles has been studied [1]. The system of carbon particles was processed in electrical field in polymer melt with controlled ion concentration. Phase transitions of colloidal systems of carbon particles only have provided an effective interpretation of the complex evolution of the self-assembled structure of carbon particles. Interactions between doublets of CB colloidal particles have been interpreted in terms of DIVO approximation of interaction energy of two blocks as multiples of average thermal fluctuation KT. Plots of the sum of energy of electrostatic repulsion and of energy of van der Waals attraction versus separation between the doublets show the energy barriers to coagulation of high B and the energy wells with the secondary minima of depth W. We suggest colloidal phase transitions at critical conjuncture of the concentration of ions and of the parameter of surface potential. Six transition lines enclose five phases of the assembly of carbon colloids: lateral vapor + lateral vapor (VAPOR), lateral liquid + axial vapor (COLUMNAR LIQUID CRYSTAL), lateral liquid + axial liquid (SMECITIC LC), lateral liquid + axial solid (NEMATIC LC), and lateral solid + axial vapor (SOLID). The model provides a tool to control the evolution of carbon self-assembly. For instance, the required carbon self-assembly with high specific surface area and high permiittivity for super-capacitors can be induced in appropriate electrical field in a polymer melt with effective ionic concentration. References [1] Bouda, V., Chlabek, J., Carbon Metamorphoses in a Medium with Varying Ionic Concentration. Mat. Res. Soc. Symp. Proc. Vol. 661, MRS 2001, p. KKS.17.1 - 6.

SESSION H7: FOSTER SESSION SYNTHESIS AND PROPERTIES OF 1D/2D/3D NANOSTRUCTURES
Chairs: Lhadli Merhari and David P. Taylor
Wednesday Evening, December 4, 2002
8:00 PM
Exhibition Hall D (Hynes)

H7.1
DIRECT NANOSCALE PATTERNING OF SOFT AND HARD MAGNETIC NANOSTRUCTURES VIA DIP-PEN NANOLITHOGRAPHY (DPN). Lei Pu, Vinayak P. Dravid, Dept. of Materials Science & Engineering, Xiaogang Liu, and Chad A. Mirkin, Dept. of Chemistry, Northwestern University, Evanston, IL.

Magnetic structures enjoy a wide variety of technological applications, and exhibit several basic and intriguing scientific phenomena. Other than the obvious applications of information storage, magnetic structures, especially at nanoscale, are becoming increasingly important in bio-detection, sensing and therapeutic fields. The advent of nano-fabrication technology opens up new avenues to manipulate magnetic materials, and create novel architectures for engineering new materials, devices, and for obtaining better insight into micromagnets. We have utilized the unique site-specific patterning capabilities of recently developed dip-pen nanolithography (DPN) approach to pattern soft and hard magnetic nanostuctures. This is accomplished in two distinct but related ways. First, DPN is used to pattern MHA templates that have affinity for oxide nanoparticles. Once these "sticky" patterns are created by DPN, the substrate is dipped in colloidal suspension of magnetic oxides (Fe3O4, MnFe2O4) to allow colloidal nanoparticles binding to MHA templates. In a second novel approach, sol-gel precursor for Barium ferrite (BaFe12O19) is used to directly pattern complex architecture on SiOx substrates. The precursor pattern is then directly converted to hard
Bs-hexaferrite nanostructures under appropriate heat treatment. A variety of structural and magnetic measurements indicate the efficacy and efficiency of the process. The presentation will cover the synthesis, patterning and characterization of magnetic nanostructures and argue that DPN-based approach present a alternate strategy for complex and hierarchical architecture for inorganic nanostructures.


Current optical based lithography is now reaching its limits of resolution, while electron beam lithography is a serial process and so is inherently slow. Therefore, methods for nano-lithography, such as, micro-contact printing (MCP) and nano-imprint lithography (NIL), that offer low cost, high throughput processes are being developed. MCP involves curing an elastomer, normally polydimethylsiloxane (PDMS), onto a master and then using this as a stamp to transfer the "ink". NIL involves imprinting the master, usually into poly(methyl-methacrylate) (PMMA) and then using the patterned PMMA as a mask for subsequent processing. Here, we report on the use of a focused ion beam (FIB) system to prepare transmission electron microscopy (TEM) cross-sections of the elastomer stamps and patterned specimens. We show that the lift-off technique can be used to prepare cross-sections of both the elastomer stamps and the patterned PMMA. As the FIB system can prepare the cross-sections to within 50 nm of a specific site this enables the same regions of the master, stamp and patterned template to be cross-secured for transfer and reproducibility to be assessed over the patterned area. The masters were prepared using a combination of e-beam lithography and conventional processing. The sample beam elimination system (SEES) was used as the elastomer and PMMA for the nanoimprint.

H7.3 FROM SELF-ORDERING TOWARDS IMPRINT LITHOGRAPHY: LARGE-SCALE SYNTHESIS OF MONODISPERSNE NANORODS. Konstantin Nischel, Jesual Choi, Ifad E. Wemphoven, Herbert Hofmeister, and Ulrich Gösele, Max-Planck-Institute of Microstructure Physics, Halle, GERMANY; Guido Sauer, Georg Beduhn, and Siegfried Schneider, Institute of Physical Chemistry, University of Erlangen, GERMANY.

Monodisperse nanorods are highly desirable for many biomedical applications ranging from diagnostics of cancer cells to drug delivery. In the recent year, self-ordered alumina pore channel arrays, based on an approach of Masuda et al. [Science 293, 268, 1996], have attracted a lot of interest as a template material for the synthesis of anisotropic nanoparticles with a defined diameter (±10%). In analogy to polycrystals, the pore channels are hexagonally self-arranged in domains. In these pore arrays, numerous lattice defects and domain boundaries exist where large deviations of the average pore diameter occur. We introduce imprint lithography in the fabrication process of our templates, a monocrytalline arrangement of pore channels on a cm-"scale is obtained and the deviation of the pore diameters is kept below 5% in single domains. We have developed a novel e-beam imprint stamp consisting of hexagonal convex pyramid array based on modern VLSI processing using DUV-lithography, anisotropic etching, LCP, and wafer bonding. Using a commercial oil press the pattern of the imprint mold is directly transferred into polished aluminum substrates. Subsequently, the aluminum is anodized and a perfectly arranged array of highly monodisperse alumina pore channels is formed. The alumina templates are filled by electrodeposition or autocatalytic deposition with metals like Ag, Au, Cu, Cr or Ni and - in contrast to most publications in this field - a degree of pore filling of almost 100% was achieved. The nanorod diameter (20...400 nm) and its length (0.2...50 µm) can be adjusted precisely over a large range. TEM characterization shows that silver nanorods are single crystalline. The nanorods might be transferred into an aqueous solution by selectively dissolving the alumina matrix. The dissolved nanorods can be further functionalized or serve as templates for hollow polymer nanococoonas.

H7.4 FORMATION OF CARBON NANOTUBES ON NICKEL FILMS/PARTICLES USING CVD. Stefano Barbieri and Al Sacco Jr., Center for Advanced Microgravity Materials Processing, Department of Chemical Engineering, Northeastern University, Boston, MA.

Carbon nanotubes (CNTs) are a possible material for field emission. One problem is that nanotubes are often produced from metal particles embedded in non-conducting surfaces (e.g., alumina/alumina). This requires rearranging the nanotubes on a conducting surface for application. CNTs can be produced on a conducting media using CVD and thin film nickel supports. CNTs were grown on thin nickel films of thicknesses 5 nm. Thin nickel films were produced by evaporation at 5 x 10^-4 torr. The films were then exposed to flowing hydrogen (20 mL/s, STP) at 1178 K. Their initial thickness controlled the height and the diameter of the semi-hemispherical particles (sitting on a continuous nickel film) resulting. As the thickness of the thin-film decreased from 5 nm to 1 nm, the height of the nickel particles decreased from 16 nm to 2 nm ± 10%, and the diameter decreased from 80 nm to 7 ± 45 nm ± 10%. These nickel particles were exposed to a mixture of 5 gases including H₂, CO, CO₂, and H₂O at 20 mL/s (STP) at 500 K and 1 atm. The gas phase carbon activity (a₃) was controlled at 10, while the atomic ratio C/H in the gas phase was set at 0.1. SEM indicated that CNTs were observed on all samples. As the height and diameter of the particles became smaller, the diameter of the nanotubes decreased from 40 nm to a minimum value of approximately 20 nm ± 1.5 nm, at which point the density of nucleation diminished. Increasing (a₃) to 20, while the other parameters remained constant, increased the nucleation size and decreased the minimum diameter of the carbon nanotubes to 15 nm ± 1.5nm. This suggests that control of the thermodynamic driving force for carbon deposition coupled with control of particle size can be used to generate uniform nanotubes for electron emitters.

H7.5 SYNTHESIS AND CHARACTERIZATION OF CATALYST-FREE CARBON NANOTUBES FROM SILICON CARBIDE PRECURSORS. Elen S. Humphreys, John B. Vander Sande and Yut-Ming Chiang, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Catalyst-free carbon nanotubes have been produced by the high temperature active oxidation of SiC. By selecting thermalchemical conditions that promote the volatilization of SiC while maintaining local equilibrium in the graphite stability field, carbon nanotubes can be nucleated and grown from a variety of SiC precursors. In this study we used SiC powders of various particle sizes, and showed that under suitable thermalchemical conditions, particles of up to 10 micrometer diameter can be completely converted to densely-packed arrays of multivall nanotubes. The resulting materials have been characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. These novel high-purity materials are found to contain a high proportion of aligned multi-walled carbon nanotubes with narrow diameter distribution between the 2-10 nm range. Raman spectroscopic characterization of these high purity nanotubes, and their use in chip packaging, are the topics of two other papers at this meeting. This research is supported by ONR Grant No. N00014-98-1-0384 and the DuPont-MIT Alliance.

H7.6 SIMPLE USE OF SiO₂ FILM THICKNESS FOR THE CONTROL OF CARBON NANO-TUBE DIAMETER DURING FERROCENE CATALYZED CVD GROWTH. Nitin Chopers, Bruce Minds, Dept. of Chemical and Materials Eng., University of Kentucky, Lexington, KY; Padmaker Kichambare, Rodney Andrews, Center for Applied Energy Research, University of Kentucky, Lexington, KY.

Selective growth of carbon nano-tubes (CNT) on silicon oxide (SiO₂) patterned substrates has been accomplished by taking advantage of the non-reactivity of ferrocene catalyst on alumina or H-terminated Si surfaces in a CVD process (Dali Qian Ph.D. dissertation 2001 University of Kentucky). N. Qian et al. demonstrated here is that this phenomenon can be used to control the diameter of CNTs when sufficiently narrow lines of SiO₂ surrounding by H-terminated Si are used. The diameter of CNTs grown on 125 nm wide lines are formed at the cleared of etched face of a Si/SiO₂/Si multilayer structure. This allows the precisely controllable thickness of a SiO₂ film to determine an exposed SiO₂ line width. This is used for e-beam lithography since film thickness determines nm-scale line dimensions. CNTs are then formed by CVD with ferrocene/H₂/Ar mixture at 700°C. CNTs are observed to grow only on the exposed SiO₂ surface at the edge of the "mask" structure. CNT diameters of 13.2, 20.5, 34.2, 64.3nm are observed for SiO₂ film thickness of 12, 16, 28, and 66 nm. Standard deviations are 1.1, 1.4, 1.4, 1.7 respectively. The larger distribution of CNT diameter with increased line width is consistent with wider SiO₂ linewidths not being able to affect smaller nucleation centers. Further investigations show improved control of diameter with etching technique as well as the successful use of self-assembly chemistry of iron catalyst for non-ferrocene catalyzed CNT growth by CVD. Resultant CNT diameter is directly related to catalyst support size. CNTs growing from this "mask" edge geometry have applications for interconnections, NEMS or can be removed for later self-assembly into chemically defined structures.

H7.7 FIB-ASSISTED Pt DEPOSITION FOR CARBON NANOTUBE INTEGRATION AND 3-D NANOENGINEERING. K. Do, J. Rullan, K. Dunn, R. Moore, F. Heuchling. University at 168
Carbon nanotubes (CNTs) are potential candidates for a variety of new types of devices and some interconnect applications. High mechanical strength, light weight, good thermal and electrical conductance, and a range of attractive electrical properties make CNTs particularly interesting building blocks for rapidly emerging nanoelectronics and nanomechanics. For nanoscale devices based on carbon nanotubes, the performance will be critically dependent upon the quality of the interfaces, since the entire device may now lie within nanometers of the interface. Successful integration of the nanotubes with metal aiming for application as an active part of a device or as a nano-wire, requires understanding of the effects of the metal/fabrication process on the structure and chemistry of the nanotube, and in the stability of the CNT-metal interfaces. A focused ion beam (FIB) instrument can be used to fabricate ultra-thin metal lines on carbon nanotubes to measure electrical properties or for integration and nanoelectronic purposes. The quality of the interface between CNT and the metal contact is of high interest, as the 30 kV focused Ga ion beam of the FIB can produce sufficient surface modification to affect the future device performance. We have used the FIB instrument to fabricate the metal contacts and to make the electron-transparent samples across the Pt/CNT structure for further studies via transmission electron microscopy. Auger electron spectroscopy was used to characterize the composition of FIB-fabricated metal lines. The initial stages of Pt-assisted Pt deposition on multi-wall carbon nanotubes (MWCNTs) by focused ion beam (FIB) deposition were monitored by transmission electron microscopy (TEM), electron energy loss spectroscopy, and energy filtered TEM. The effects of Pt deposition on the shape and composition of the topmost CNT layer and the function of FIB imaging and deposition parameters are presented. FIB parameters are optimized to provide the non-destructive imaging and controlled Pt deposition with minimal damage to the CNT.

H7.8 GROWTH OF WELL-DEFINED CARBON NANOTUBES ON ATOMIC FORCE MICROSCOPY PROBES SUITABLE FOR METROLOGY APPLICATIONS. Y.N. Emirov, J.D. Schumacher, M. Benkob, University of South Florida; D.A. Walters, University of Central Florida; Z.F. Ren, Z.P. Huang, Boston College; B.B. Rosie, Agere Systems; and B. Schrief, University of South Florida.

Well-defined carbon nanotubes (CNT) were grown on the apexes of standard Si atomic force microscopy (AFM) probes for high aspect ratio critical dimension measurement (CDM). Their mechanical strength at small diameters makes them ideal probes for narrow and deep features. For these applications growth location, diameter, length and orientation of the CNT needs to be precisely defined. Already existing manually attached designs and CNT grown by standard chemical vapor deposition cannot satisfy these requirements. Our efforts demonstrate that the application of advanced focused ion beam (FIB) techniques in conjunction with plasma chemical vapor deposition (PCVD) offers a possible solution for achieving above design goals. Due to the interesting mechanical and electronic properties of CNT, this technology could be utilized beyond AFM probes such as the development of CNT integrated electronic circuits or micro electromechanical devices (MEMS).

H7.9 BUILDING MACRO-SCALE NETWORKS AND BRIDGES OF ALIGNED CARBON NANOTUBES. Anynu Cao, Bingbing Wei, P.M. Ajayan, G. Ramanath, Dept of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, NY.

In order to harness the attractive properties of carbon nanotubes (CNTs) for future device applications, it is essential to create monolayer architectures with CNT-metal contacts. Here, we demonstrate two bottom-up methods based on thermal chemical vapor deposition (CVD) to assemble cm-scale networks of mm-wide CNT stripes, and mm-scale bridges of aligned carbon nanotubes (CNTs) across metal contacts. Both methods are attractive for creating CNT-based multilayer and crossbar architectures, and are easily amenable to scaling to lower device dimensions as well as larger areas. In the first method, we use a two-step CVD process in which a patterned CNT film serves as a template for growing cm-long mm-wide CNT stripes. Track patterns of exposed silica are created in a blanket film with vertically aligned CNTs grown from a xenon/ferrocene mixture. In the second step, vertically oriented CNT stripes grow in these exposed regions and inherit the pattern configuration. The CNT template can be selectively removed while retaining the crossbar-like networks of CNT stripes. In the second method, we use mm-scale bridged cm-long multilayered CNT bundles across metal contact structures. CNT bundles (average diameter < 50 nm) are synthesized by CVD from a hexane-ferrocene-thiophene mixture. Each bundle consists of tens to hundreds of aligned CNTs. During the CVD process, the as-grown nanotube bundles are carried by gas stream to the end of the reaction quartz tube, where they deposit onto arrays of relief metal structures on silicon substrates and form macroscopic bridges. We show that the CNT bridges assemble acroisolated metal islands in seconds. The post and telephone-pole type configurations are aligned along the gas flow direction.

H7.10 VERTICAL ALIGNMENTS OF SINGLE-WALLED CARBON NANOTUBES ON CHEMICALLY FUNCTIONALIZED SILICON SUBSTRATES. Ha Jin Lee, HyeYoung Park, Sunyoung Koo, Hyoung Lee, Hanyang University, Department of Chemistry, Seoul, KOREA.

A carbon nanotube has been widely investigated as an essential component for fabricating nanoelectronic devices and its numerous applications. We investigated the vertical alignments of single-walled carbon nanotubes (SWNTs) on chemically functionalized Si substrates using chemical reactions between chemical groups in SWNTs and surfaces. For controlling the high selectivity of a specific chemical reaction, a pre-patterned 3-D nanostructure was used by using AFM nanodotification lithography for achieving the vertical alignment of SWNTs. To consider the further chemical reaction with chemically modified Si surface, the carboxylic acid groups were converted into acid chloride groups followed by the reaction with chemically functionalized surfaces. The protruded structures on pre-patterned areas strongly suggest the vertically aligned SWNTs, and the distribution of the vertically aligned SWNTs and their heights are longer on the prolonged reaction time. The aspect ratio of SWNTs aligned on Si enabled functionalized surface is independent from the reaction time (H/W < 0.2). After random alignment of relatively shorter nanotubes on the substrate, their bundle size increases with increasing the reaction time due to strong van der Waals interaction between the lateral axes of nanotubes described as "nucleation growth". Longer tubes get also adsorbed on the surface by increase in the bundle size and nanotube length, simultaneously. Based on the chemical reactions of the modified SWNTs with chemically functionalized surfaces, selective attachments of SWNTs were carried out onto pre-patterned surfaces. Detailed characterization of aligned SWNTs will be discussed.

H7.11 CONTROLLED DEPOSITION AND APPLIED FIELD ALIGNMENT OF SINGLE-WALLED CARBON NANOTUBES FOR CNT DEVICE FABRICATION. Ian Smith, Lockheed Martin Space Operations, Hampton, VA; Buzz Wincheski, NASA Langley Research Center, Hampton, VA; JoAnne Ingram, Swales Aerospace, Hampton, VA; Neal Watkins, Swales Aerospace, Hampton, VA; Jeffrey Jordan, NASA Langley Research Center, Hampton, VA.

Carbon nanotubes (CNTs) offer great potential for advanced sensing devices due to their unique electronic transport properties. However, a significant obstacle to the realization of practical CNT devices is the formation of controlled, reliable and reproducible CNT to metallic contacts. In this work, a procedure for the deposition and alignment of CNTs onto metallic electrodes using chemically functionalized lithographic patterns is reported. This method uses photo and electron beam lithography to pattern simple Cr/Au thin film circuits on oxidized Si substrates. The circuits are then re-patterned with a self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTES) to specify desired CNT locations between electrodes. The application of an applied electric field to the metallic contacts during the deposition of solution suspended single walled CNTs causes alignment of the CNTs in the field direction. This method consistently produces aligned CNTs in the defined locations. Application of this deposition method to the fabrication of CNT based sensor material is also presented.
Creating hybrid molecular units consisting of different kinds of nanoscale blocking, tunneling, and building blocks is of great interest for building electronic devices and networks. Carbon nanotubes (CNTs), linked with nanoclusters in a striking example of such a unit that will allow the exploration and tuning of unique electronic and/or optical properties of nanotubes and 3D quantum dots. Here we demonstrate for the first time using high resolution transmission electron microscopy (HRTEM), optical absorption spectroscopy (UV-Vis), and Fourier transform infrared transmission spectroscopy (FTIR) the attachment of Au nanoclusters to CNTs via hydrophobic interactions between self-assembled molecular monolayers of octanethiol molecules capping the nanoclusters, and acetone molecules activating nanotubes surfaces. HRTEM and OS measurements show that interlinked assemblies of Au nanoclusters with average size of ~3 nm are attached to the multivalved CNTx treated with acetone. The Au nanoclusters retain a strong surface-plasmon peak after attachment and repeated washing, indicating robust interlinking and the preservation of the optical and electronic properties of the nanoclusters. These assemblies have discrete intercluster spacings with a preferred length corresponding to about one to two times the length of the octanethiol molecule, suggesting molecular interdigitation. This and the decreased flexibility of the octanethiol, indicated by FTIRs, indicate strong hydrophobic interactions with the surrounding octanethiol molecules and acetone adsorbed on the surface. Results of our experiments with CNTs that were not treated with acetone showed no observable cluster attachment, emphasizing the importance of surface chemistry of the CNTs to create hybrid structures using molecular connectors. Based upon these results, we present a phenomenological model to explain the salient features of hydrophobically linked nanocluster-nanotube hybrid molecular units and assemblies.

H7.15 NANOSTRUCTURED MATERIALS ON CARBON NANOWALL TEMPLATES. Yihong Wu, National University of Singapore, Dept. of Electrical and Computer Engineering, Singapore and Data Storage Institute, SINGAPORE; Bingxin Yang, National University of Singapore, Dept. of Physics, Singapore and Data Storage Institute, SINGAPORE.

Recently we have succeeded in growing well-aligned two-dimensional carbon nanostructures dubbed carbon nanowalls. The nanowalls exhibit a remarkably different surface morphology as compared to fullerences and carbon nanotubes, in particular their two-dimensionality and high surface area. Under typical growth conditions, the as-grown nanowalls can have a thickness of several nanometers, a width of sub-micron, and a height of several microns. In-between the nanowalls there exist empty spaces of sub-micron dimensions. The unique surface morphology of carbon nanowalls makes them an ideal template for fabricating a class of mesoscopic materials which may have applications in batteries, gas sensors, catalysis, and light emissions / detectors, field emission and biomedical devices. The results on the growth of Ni, NiCoFe, Fe, ZnO / TiOx, InOx, SiO2, Au, Cu, and other materials will be reported in the meeting. All these materials form conformally on the nanowalls, resulting in pseudo-3D nanostructures. The application of some of these materials as gas sensors and electrodes for supercapacitors is also being explored.

H7.16 EFFECT OF SITE DENSITY OF ALIGNED CARBON NANOTUBE ARRAY ON ELECTRIC FIELD SCREENING. Yi Tu, Zhongqing Huang, Deshi Wang, Zhifeng Ren, Dept. of Physics, Chestnut Hill, MA.

Electric field screening has been observed in the densely packed carbon nanotube arrays. In this report, we show that CNTs arrays with different site density have been grown from Ni dots made by electrochemical deposition by plasma-enhanced chemical vapor deposition. Field emission properties of CNTs arrays with site density from 103 to 107/cm2 and length of 1, 5, 10 µm have been studied.

H7.17 Abstract Withdrawn.


Recent progress in carbon nanotube synthesis has made it possible for a carbon nanotube to be grown vertically, as well as laterally, on a substrate at designated sites, making possible application of carbon nanotubes as nanoelectronic components. However, there is a drawback in carbon nanotubes, which limits application to large-scale integrated devices. Although a method has been reported to selectively destroy metallic nanotubes, leaving only semiconducting ones, there is no known method of controlling the chirality of carbon nanotubes during synthesis, making it difficult to select semiconducting carbon nanotubes with a fixed energy gap for high-density integrated circuit application. Therefore it may be useful to have a device that does not rely on the transport properties of the carbon nanotubes but still delivers switching capability with gain. One such device is the carbon nanotube gated field emitter. It utilizes the geometric enhancement of the nanotube tip structure and the high current density transport capabilities of the carbon nanotubes. Here we report on the fabrication and operation of a lateral carbon nanotube field emitter. Compared to vertical field emitters using carbon nanotube cathodes, it has less alignment problems since the anode is fabricated at the same time as the cathode and the gates, and also may have reduced leakage since the electrodes are separated. We used thermally oxidized Si as the substrate. Initially, Cr/Au alignment marks are deposited to use as reference markers. Then a thin layer (50 nm) of Al is evaporated, which will act as the sacrificial layer. Multi-wall carbon nanotubes (MWNTs) were synthesised by plasma-enhanced chemical vapor deposition and dispersed on the surface. Electron beam lithography is used to define the anode, gate, and the cathode contacts of the device. After Cr/Au metal deposition and lift-off the sacrificial Al is etched away leaving the nanotubes suspended. The device operating voltage is ~11 V. The emission characteristics exhibit Fowler-Nordheim behaviour, which is a strong evidence of field emission. We will further investigate the characteristics of gate dependent operation of the device and also look at the performance of the devices with differing dimensions and carbon nanotube diameters.

H7.19 FIELD EMISSION FROM RUTHENIUM CONTAINING MULTIVALLED CARBON NANOTUBES. Radoslaw Kichansky, Dali Qiao, David Jacques, Rodney Andrews, University of Kentucky, Center for Applied Research, Lexington, KY.

Among the types of materials investigated for field emitters, multiwall carbon nanotubes (MWNTs) are well suited for display applications as their structure lends itself easily to fabrication on nanometer scale. Hence, tremendous efforts are being directed to achieve high electron emission current density at low applied voltage from the MWNTs. However, the poor emission current stability of MWNTs has hampered their potential as field emission display devices. One of the easiest way of improving emission current stability would be the doping of the MWNTs. We report on the growth and field emission properties of Ru containing MWNTs, prepared by chemical vapor deposition (CVD) on Si(100) substrates. A mixture of ferrocene and ruthenocene (6:1) in xylene was used for the growth of Ru containing MWNTs. Scanning electron microscopy (SEM) reveals that Ru containing MWNTs are quasi-aligned with thicker root ends (outer diameter ~ 40 nm) and thinner tip ends (outer diameter ~15 nm). Some of these nanotubes form multi-wall tube chain structures in which the second segment grows from the tip of previous segment. The characteristic current-voltage measurements of Ru containing MWNTs demonstrate a low turn-on field of 11 V/µm. The field emission current density in excess of about 14 mA/cm2 at an applied field of 20 V/µm has been achieved. A stable emission current density under a constant applied voltage has been observed. These investigation indicate that Ru containing MWNTs film could be a very promising for field emission devices.

H7.20 Zn1-xMgₓO NANORODS VIA MOLECULAR BEAM EPITAXY. Young Woon Hoo, V. Vardarajan, K. Kim, Michael Kaufman, David Norton, University of Florida, Dept. of Materials Science and Eng., Gainesville, FL; Matthew Chiabotto, Solid State Div., Oak Ridge National Laboratory, Oak Ridge, TN.

We recently reported on the growth of single crystal ZnO nanorods using catalyst-driven molecular beam epitaxy. ZnO nanorods are a growth on a SiO2-terminated Si substrate surface. In that work, we will describe recent results for the growth of the Zn1-xMgₓO nanorods. The modulation of the bandgap in compound semiconductors is a key issue in heterojunction formation for electronic and optical devices. In epitaxial thin films, the bandgap of ZnO (Eg=3.37eV) can be modified by alloying with MgO. Photoluminescence of Zn1-xMgₓO nanorods shows a peak shift to higher energy with increasing Mg, indicative to an increasing bandgap. The synthesis and properties of these structures will be reported, including photoluminescence, microstructure, and TEM data. The site-selective, in situ formation of ZnO-reinforced nanowires and nanorods may prove attractive for nanodevice concepts.
H7.21 
ZnO NANOWIRE GROWTH ON VARIOUS SUBSTRATES BY CVD THROUGH LIQUID-TO-LIQUID CRYSTAL GROWTH MECHANISM. Hyun-Gi Hong, Jung Iim Sohn, Youn-Su Kim, Seonghoon Lee, Department of Materials Science and Engineering, Kwangju Institute of Science and Technology (K-JIST), Kwangju, KOREA.

We have grown zinc oxide nanowires on silicon, mica, and gallium nitride substrates by thermal chemical vapor deposition (CVD) and investigated their structural and optical properties, using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and photoluminescence (PL) spectroscopy. The Au catalyst metal films are deposited on various substrates by a pulsed laser deposition technique under a pressure of 9×10⁻⁴ Torr. We found that the metal thin film was broken to nanoparticles during the CVD growth. Controlling the size of nanoparticles, we adjusted the diameter of nanowires. We generated zinc and oxygen vapor through carbothermal reduction reactions and deposited on substrates with a vapor transport process via catalyzed crystal growth at a temperature of 900°C or 950°C through vapor-liquid-solid crystal growth mechanism. The orientation of ZnO nanowires showed strong dependence on substrates. We investigated the dependence of the orientation and alignment of ZnO nanowires on a substrate, using SEM and TEM. Especially, gallium nitride substrate among substrates we used, is good for aligning zinc oxide nanowires. The size of ZnO nanowires is 20 to 100 nm in diameter and a few micrometers in length. From the statistical analysis, we found that ZnO nanowires are a wurtzite structure. PL spectra of ZnO nanowire were measured with a HeCd laser (325 nm) of excitation power of 20 mW. Strong band gap edge emission at 375 nm with a full width at half maximum (FWHM) of 52.09 meV was observed.

H7.23 
CONDUCTING NANOWIRES AND NANOTUBE MATERIALS PREPARED FROM POLYMER FIBER TEMPLATES. Hong Dong, Voorad Nyame, Frederick Ochanga, and Wayne E. Jones Jr., Chemistry Department and Institute for Materials Research, State University of New York at Binghamton, NY.

The preparation of well-defined nanomaterials using template methods is well established in the materials literature including porous ceramics, open-framed layered structures, and thin films. In an effort to develop novel thermally and electrically conducting materials, we have recently prepared extremely low dimensional conducting nanowires and fibers from conducting polymers (e.g. polyaniline, polypyrrole) using electrospinning, non-mechanical "electrospinning" method. Insulating Poly(L-lactide) (PLA) fibers with average diameter of 200-700 nm were initially fabricated as core material. The fibers were subsequently coated with thin 50-100 nm films of polyaniline or polypyrrole by in-situ polymer deposition methods. Upon relatively mild thermal treatment under inert atmosphere the PLA core fibers decompose leaving conducting tubes as demonstrated by SEM. The greatly enhanced surface to volume ratio of these materials is predicted to yield enhanced sensitivity compared to the thin films prepared on substrates. Further, using more aggressive thermal treatments or the application of electroless plating stable conducting nanotubes of metals (e.g. Au, Cu) or graphite can be prepared suitable for use as thermal or electrical conductors in nanodevice applications.

H7.24 
THERMOELECTRIC NANOWIRES BY TEMPERATURE SYNTHESIS: FABRICATION, CONTACTS AND PROPERTIES. Oded Rubin,*, Yu-Ming Lin*, Stephen B. Cronin*, Gang Chen*, Mildred S. Dresselhaus**, Massachusetts Institute of Technology, *Dept. of Chemistry, **Dept. of Electrical Engineering and Computer Science, **Department of Physics, and *Dept. of Mechanical Engineering, Cambridge, MA.

Using the technique we have developed to grow porous alumina templates on the surface of silicon wafers, we have fabricated arrays of nanowires of thermoelectric materials. By this method we can control the in-plane-phase by the design of the template and the substrate, and the out-of-plane dimension by control over the electrochemical nanowire growth process. We use several straightforward methods to make electrical contacts to the nanowires. Our transport studies show that both the structure of the nanowire and the contact region have a strong influence on the observed properties of the arrays.

H7.25 
Abstract Withdrawn.

H7.26 
RATIONAL CONTROL OF NANOSCALE HELICAL MORPHOLOGIES THROUGH BINARY SELF-ASSEMBLY. George John, Jong Hwa Jung, Kaname Yoshida, Hiroyuki Miyahikawa, Toshimi Shimizu, CREST, Japan Science and Technology Corporation, Nanotechno Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

Mixed components of cardanyl glucoside derived from renewable resources provided nanotubes on self-assembly in water while the saturated homologue generated twisted fibril morphology. The cardanyl glucoside mixture was fractionated into individual four components to study their contribution to the nanotube formation. The rational control of self-assembled helical morphology has been achieved by binary self-assembly of the saturated and monoene derivatives. This method can provide the generation of a diversity of self-assembled high-aspect-ratio nanostructures (HAs), ranging from twisted, ribbons, helical ribbons and nanotubes.

H7.27 
SYNTHESIS BY SELF-ASSEMBLY OF IRON-COBALT NANOALLOYS. Melisa Zuber, Rina Tannenbaum, Georg Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

Nanoalloys, i.e. alloys formed via the co-aggregation of different metals at the nanoscale, represent an exciting new area in nanotechnology. These nanoalloys have unique properties that neither the bulk alloys, nor the discrete atoms possess. Gold and silver nanoalloys have been used to produce nanoalloys, but no such systems have yet been reported with transition metals. In this paper we are proposing the synthesis of iron and cobalt nanoalloys via the co-decomposition of iron and cobalt carbonyls. Zero-valent iron and oxide clusters that are produced via this decomposition exhibit excellent magnetic properties. Combining these iron nanoalloys with cobalt nanoclusters will form new nanoalloy compositions with good magnetic properties and interesting potential applications. In order to form iron-cobalt nanoalloys with no preferential aggregation of metal atoms resulting in phase segregation, the decomposition kinetics of the iron pentacarbonyl and dicobalt octacarbonyl precursors had to be firmly established. The kinetics of cobalt cluster formation via dicobalt octacarbonyl decomposition have been thoroughly investigated, but data for iron-pentacarbonyl decomposition is relatively scarce. To fully understand the formation of the iron nanoalloys, a kinetic study was performed varying carbonyl concentrations and reaction solvents in order to establish reaction order and rate constants. This decomposition was performed in the presence of a polystyrene matrix, since the polymer attaches to the surface of the cluster, restricting the amount of metal-metal interactions that may occur, thus limiting cluster size. The studies presented in this work have established this decomposition to be a higher order process (not first order as previously assumed), with a complicated intermediate mechanism, which has been experimentally verified. By using this kinetic data, we will be able to predict the necessary conditions for the creation of new in-situ iron-cobalt nanoalloys using carbonyl precursors.

H7.28 
ORGANIC MOLECULES ACTING AS TEMPLATES ON Cu(110). Federico Rossi, V. Naitoh, M. Schunack, E. Lefebvre, G. Stengard, and F. Bensenbacher, Physics Department and iNANO, University of Aarhus, DENMARK, P. Jingga, A. Gourdon, and C. Joschin CEMES - CNRS Toulouse, FRANCE.
Large organic molecules have recently attracted interest from a fundamental point of view and for prospective applications in nanoelectronics, as these molecules can act as building blocks for molecular electronics devices [1]. We investigated the adsorption of Lander molecule [2] (C9H10Br8) on Cu(110) by Scanning Tunneling Microscopy (STM) (Fig. 1). The Lander molecule has a central polyaromatic molecular wire (conducting backbone), and four "spacergs" (3,5-di-tert-butylphenyl) for isolation from the substrate. The four legs are imaged with 2 different conformations by STM. Manipulation experiments with the STM at low temperatures on irradiated Lander molecules adsorbed on step edges reveal a restructuring of conformations [3]. When retracted from a step, a step-like nanostructure appears. The structure's width is two atomic rows, corresponding to the distance between the spacer legs within the molecule. The process is thermally activated, repeating the same manipulation on molecules adsorbed at low temperatures (150 K), no restructuring of the Cu step edges is found. In a second set of experiments, the Lander (110) surface was exposed to oxygen to form oxygen-induced (2x1) reconstruction surface. By dosing a proper amount of O2 at 350°C we nanopatterened the substrate into Cu troughs along the [001] direction with 2 nm width, with a periodicity of about 8 nm. When Lander molecules are deposited on this template, they preferentially adsorb on bare Cu regions. By tuning molecular coverage in a controlled manner, we obtained long rows of 1D molecular nanostructures. This type of forced self-assembly opens new possibilities for ordering organic molecules on surfaces. [References: 1] C. Joachim, J.K. Gimzewski and A. Aviram, Nature 409, 541 (2001); R. Reiss et al. (Nanolab) as templates on Metal Surfaces, Science 296, 528 (2002).

H7.29
SELF-ASSEMBLY OF METAL-OXIDE NANOSTRUCTURES: OXIDATION OF Cu FILMS BY IN-SITU UHV-TEM.

Chi-Chun Zhou, Judith C. Yang, Materials Science and Engineering Dept, University of Pittsburgh, Pittsburgh, PA.

The universal response of metal surfaces exposed to oxygen-bearing atmospheres is to oxidize. The oxidation product may be a thin protective adherent film or oxide islands depending on the oxidation conditions. The structural changes of the oxides are dependent on the complex kinetics and energetics of the particular materials system and the oxide morphology is controlled by kinetic and thermodynamic factors during the processes of oxidation. This order of analysis provides insights into distinguishing between morphologies due to kinetic or thermodynamic considerations. It is reasonable to expect that temperature would affect the kinetics of oxidation of Cu(110) and modeled some of the morphological changes. We demonstrated that dramatically different morphologies of oxide structures can be achieved by modifying the oxidation temperature. Three-dimensional islands up to 150 nm in diameter were formed on Cu(100) surfaces. The oxide volume increases parabolically before the shape transition, and exponentially afterward. The oxidation process is divided into two stages: the primary pyramidal structure, hollow CuO terrace-pyramids, was formed when we oxidized Cu(100) films with thickness of 700 Å at temperature of 1000°C. Therefore, formation of terraces and space within the pyramids results from the sliding of the blocks of the island over one another on the slip system of [111][01] to release the compressive strain exerted on the island due to the large volume change accompanied with oxidation of Cu to CuO.

H7.30
A GENERALIZED FLUID-FORMING METHOD FOR SELF-ASSEMBLY OF PARTICLES INTO PLANAR ARRAYS.

X. Liu, Dept of Ceramic and Materials Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ; E.F. McCandlish, Ceramart Corporation, New Brunswick, NJ; F. Coanday, K. Miyahara, Dept of Ceramic and Materials Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ; L.E. McCandlish, Ceramart Corporation, New Brunwick, NJ; R.E. Riman, Dept of Ceramic and Materials Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ.

Self-assembly of objects with different sizes and shapes into complex systems has excellent potential for application in microelectronics, optics, magnetics and microelectromechanical systems. We have developed a fluid-forming process for self-assembly of particles into planar arrays. The process operates on particles whose sizes range from nanometers to micrometers. Particle morphology can be used to control the orientation of the particles within the arrays. For oriented-particle arrays, we have explored the use of cube-shaped particles. Randomly-oriented particle arrays can be processed using spherical particles. All of these fluid-formed arrays can be transferred onto a wide range of substrates to make monolayer or multi-layer structures. This presentation focuses on the preparation of <001>-oriented Pb(Zr Ti)O3 arrays using cube-shaped particles. Field emission scanning electron microscope (FESEM) and imaging analysis results show that the cube arrays contained dense-packed (~80-90%) particles in the x-y plane. High-resolution X-ray diffraction (HRXRD) analysis and electron backscatter diffraction (EBSD) analysis revealed the crystallographic orientation of the cube particles, which were found to be randomly oriented in the x-y plane with their <001> directions oriented along the normal plane. These dense-packed <001>-oriented Pb(Zr Ti)O3 planar arrays can further be processed as textured composites or textured single-phase materials.

H7.31
THE DEVELOPMENT OF THE CONTROL OF MORPHOLOGY TITANIA BASED PHOTONIC BANDGAP STRUCTURES.


Recently, mono-sized spherical titanias has been been interest of acid catalysts for photonic band gap due to their large refractive index in the optical range (~5.5). In order to obtain the photonic crystal the particles need to be grown with as little as 5% error. They are typically assembled into photonic band gap structures (e.g., FCG) by self-assembly processes using to the powder particles. Self-assembly processes, sedimentation growth or electrostatic interactions. Therefore, there is a need of controlling the size and shape of these oxide materials. In this research we present the morphology control of titanium by wet chemical methods as so as to produce spherical sub-micron and micron size titanias. The method of preparing these materials and characterizing by SEM and light scattering methods will be discussed.

H7.32
THE IMPORTANCE OF NOTHING IN NANOARCHITECTURE.


The innate pore-solid architecture of aerogels, which are low density, insatiably nanoscale, highly porous materials, fills high surface area for heterogeneous reactions with a continuous, porous network for rapid diffusion flux of reactants and products. These advantages have previously been explored with aerogel-derived heterogeneous catalysts, but they are also relevant for sensors and for electrocatalysts where the aerogel can be made electrically conductive. Conductivity can be achieved by synthesizing conductive oxides, such as manganese or copper or conformal deposition of nanowires atop the non-conductive network of a silica aerogel. We have also developed a flexible and general synthetic route in which silica (or in some instances, titanias) sol serves as a nanogel to produce a diverse range of composite aerogels incorporating particulate guests ranging in size over six orders of magnitude from a nanometer, which is thinner than the domain size of the silica, to a millimeter) can be accommodated in the aerogel host. The chemical nature of visible guests range from metal to metal oxide, carbon, ceramic, and semiconductor to polymeric and biomolecular. The resulting composite is a material in which each phase can be independently tailored as needed. A hierarchical architecture with all the appropriate reaction, electrical, electrochemical, bioactivity, or catalytic requirements, including high surface areas readily accessed by molecular reactants, may now be assembled on the benchtop.

H7.33
SYNTHESIS AND PROPERTIES OF HYDROGEL CRYSTALS.

Xihan Liu, Zibing Hu, University of North Texas, Dept of Materials Science and Physics, Denton, TX.

Novel hydrogels with mesoscopic crystal structures have been synthesized and characterized. First, monodisperse N-isopropyl-acrylamide (NIPAAm) co-2-hydroxyethyl acrylate (HEA) hydrogel nanoparticles were made using emulsion polymerization. And then hydrogel crystals were created by covalently bonding the self-assembled nanoparticle units using crosslinker divinylulfone (DVS). The inter-nanoparticle covalent bonds contribute to the stability of crystal structure, while self-assembly provides crystal structures that diffract light, resulting different colors. As a result, the novel hydrogel crystals, which contain up to 98 wt% water, display a striking iridescence like precious opal but soft and flexible like gelatin. The novel nanostructured hydrogels demonstrated the good mechanical...
strength and thermal stability of crystal structures. The hydrogel crystals may find applications in many areas such as sensor, display, and biotechnology.

**H7.34** DEVELOPMENT OF METAL-SILICA NANOCOMPOSITES IN A SINGLE STEP PROCESS BY THE POLYMERIZABLE COMPLEX METHOD. E.R. Leite, N.L.V. Carroce, E. Longo, J.F.R. Bisches and F.M. Pontes, CEMIGMCE-LBIC, Departamento de Química, UFSCar, Sao Carlos, SP, BRAZIL; A. Barison, A.G. Ferreira, Departamento de Química, UFSCar, Sao Carlos, SP, BRAZIL; J.A. Varella, Instituto de Química, UNESP, Araraquara, SP, BRAZIL.

This work presents the synthesis and characterization of SiO₂-metal (Ni, Co, and Fe) nanocomposites processed by the Polymerizable Complex Method. The polymeric precursor solutions obtained were characterized by means of FT-Raman and ¹³C NMR spectroscopy. The results show the formation of a hybrid polymer with carbon and silicon in the macromolecular chain and the transition metal cation arrested within this polymeric chain. The nanocomposites are formed during the controlled polymeric precursor pyrolysis. The reduction of the metal cation is promoted by the CO/CO₂ atmosphere resulting from the pyrolysis of the organic material. Microstructural characterization, performed by TEM and X-ray diffraction (XRD), showed that the nanocomposites are formed by metal nanoparticles embedded in a amorphous matrix formed by SiO₂ and carbon. In the SiO₂-C system, Fe₂O₃ was also detected by XRD.

**H7.35** SELF-ASSEMBLED ORGANIC/INORGANIC NANOCOMPOSITES. Byong Geol Heo, Longhai Wang, Eric Hampey, Xiaolin Ji, and Yunfeng Lu. Chemical Engineering Department, Tulane University, New Orleans, LA.

Nanoparticles with critical dimensions less than 100 nm endow materials with unique and often superior mechanical, electronic, magnetic and optical properties, which can open a new avenue to numerous advanced applications. The method of self-assembly that spontaneously assembles and organizes various building blocks into hierarchical structures via non-covalent interactions has emerged as one of the most promising techniques to the efficient fabrication of nanostructured materials. Here we report the formation of organic/inorganic nanocomposites using the methods of sol-gel process and surfactant self-assembly. This method relies on spontaneous cooperative-assembly of silicate and surfactant molecules that spatially organizes the organic and inorganic components into two- or three-dimensional ordered nanostructures. Highly ordered (e.g., hexagonal, cubic, or lamellar mesostructured) silica/polymer nanocomposites containing conjugated aryleneethynylene polymers, ethynylene polymers, or diazine polymers has been fabricated using this method. The properties of these nanocomposites have been studied using different techniques and the results indicate that the nanostructure may endow these nanocomposites unique properties.

**H7.36** NANOPICTURE INKS FOR DIRECTED ASSEMBLY OF 3-D PERIODIC STRUCTURES. Qi Li, Gregory Grason, and Jennifer A. Lewis. University of Illinois, Urbana, IL, James Smay, Oklahoma State University, Stillwater, OK.

Nanoparticle assembly of 3-D periodic structures requires control over, and, hence, a fundamental understanding of interparticle forces, phase behavior, and structure evolution during fabrication. This talk focuses on the organization of mesoscale objects via directed assembly of concentrated nanoparticle inks. Concentrated nanoparticle gel-based inks with tailored viscoelastic properties were designed to produce 3-D structures with self-supporting features. The inks were reversibly deposited in a layer-by-layer sequence to directly write the desired 3-D pattern. 3-D periodic structures with spanning features that vary between ~100 nm and 1 mm were created from functional nanoparticle inks consisting of ferroelectric barium titanate particles (D ~ 60 nm).

**H7.37** WET PROCESS MOLECULAR PLANTING IN A SPECIFIC SITE OF SILICON WITH Si-C COVALENT BONDS. Hiroko Toda, Masato Arai, Shoji Tanaka, Institute for Molecular Science, Okazaki, JAPAN.

Alkyl monolayers anchored covalently on silicon were prepared through the reaction between 1-alkenes and hydrogen-terminated silicon (111). The 2D-patterning of the surface was done by local oxidation with an atomic force microscope (AFM) and 3D-molecular assemblies were fabricated by molecular planting in a specific site of the surface. The surfaces were oxidized with a contact-mode AFM by applying a positive bias voltage to the surface with respect to a platinum-castellated counter electrode under ambient conditions, which resulted in nanometer-scale oxidation of surfaces. The threshold voltage was 5V for anodization of silicon covered with a dodecylosyl monolayer, which was lower than that for siloxane monolayers. The alkyl monolayers showed high resistance against chemical etching and air-oxidation. The oxidized areas were etched and terminated with hydrogen atoms by NH₃-F solution, in which we could plant various molecules having C=O bonds. We planted arylamine molecules to which organic dyes such as fluorescein and porphyrin were anchored through amido-couplings. The density of fluorescence was varied depending on dopant concentration of substrates. Luminescence was very week on highly-doped silicon possibly due to effective energy transfer from dyes to substrates. The interaction between molecules and substrates will be discussed by using the well-controlled molecular semiconductor hybrid systems.

**H7.38** DENDRIMER MEDIATED 'BRICKS AND MORTAR' SELF-ASSEMBLY OF NANOPICTURES. Benjamin L. Frankqamp, Andrew R. Boal, Vincent M. Rotello, University of Massachusetts, Department of Chemistry, Amherst, MA.

Control of particle-particle spacing is a key determinant of optical, electronic, and magnetic properties of nanoparticle composite materials. We have used poly(sodium) (PAMAM) dendrimers to assemble carbonyl acid-functionalyzed mixed monolayer protected clusters (MMPCs) through acid/base chemistry between particle and polymer. IR spectroscopy and selective dendrimer staining, observed by Transmission Electron Microscopy (TEM), clearly establish that the PAMAM dendrimers are the mortar in the assembly and act to space the MMPCs in the resulting aggregates. Small-angle X-ray scattering (SAXS) was then used to establish average interparticle distances. Five generations of PAMAM dendrimer (0, 1, 2, 4, 6) were investigated and monotonically increase in interparticle spacing from 4.1 nm to 6.1 nm was observed. Initial studies involving the application of this methodology to control the magnetic properties of Mn-iron oxide nanoparticles have been completed. Mn-iron oxide nanoparticles (6.5 nm in diameter) have been assembled with PAMAM dendrimers generations 2, 4, 5, and 6. The resulting aggregates were characterized with SAXS and magnetization obtained on a superconducting quantum interference device (SQUID). An observed correlation between the blocking temperature (Tb) and the average interparticle spacing suggests that our methodology could be used to tailor the magnetic profile of the nanoparticles.

**H7.39** SELF ASSEMBLY OF MAGNETIC AND SEMICONDUCTING NANOPICTURES: BUILDING BLOCKS FOR NANO-TECHNOLOGY. Franz Redl, Stephen O'Brien, Ming Yin, Stephanie Granovarov, Columbia University, Materials Science and Engineering, Dept of Applied Physics, New York, NY; Christopher B. Murray, K.S. Cho, Glenn Held, IBM T.J. Watson Research Center, Yorktown Heights, NY.

One of the central challenges nanotechnology seeks to address is the ability of the materials components to self-assemble into complicated arrays that will have function and utility. Physical, chemical, optical, magnetic or electronic properties of nanomaterials can be tuned by adjusting size, shape and surface-chemistry. In order to take advantage of nanoscale effects we seek to control their arrangement into useful dimensions. A nanoscale approach to this issue combines the advantage of miscibility of different materials by applying solution cast methods with close vicinity in the resulting dense material (although direct contact between particles is avoided by the surfactant). We describe the formation of three-dimensional nanocrystal superlattice of magnetic iron oxide nanoparticles forming a framework of superparamagnetic spheres and semiconducting lead selenide nanoparticles. The crystals were obtained by self-assembly of the materials during co-crystallization from solution. We are exploring routes to novel synthesis of magnetic and semiconducting nanoparticles based on new materials and new inorganic chemical techniques. Iron oxide particles constitute a diverse class of materials displaying a range of optical, magnetic and catalytic properties. Ferromagnetic iron oxides have applications in magnetic storage, high frequency transformers and RF and microwave components. In addition to electronic applications the stability and biocompatibility of the iron oxides are making them leading candidates for drug delivery, diagnostic and medical imaging applications. We have worked to develop synthetic routes for the preparation of highly crystalline monodisperse nanoparticles of γ-Fe₂O₃ and are pursuing similar techniques for the other iron oxides. Fe₃O₄ (magnetite) and γ-Fe₂O₃ are both ferromagnetic making them interesting to models to explore magnetic stability and the superparamagnetic in ferromagnetic systems.

**H7.40** SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES OF Fe₃Pt₄₋ₓCoₓ NANOCOMPOSITE PARTICLES. Xiang-Cheng Sun,
dielectric loss were possible. For example, a permittivity of over 150 with a loss tangent of less than 0.1 was calculated at 1 GHz with a 10 vol% composite of nanotubes that were coated with a 5 nm thick insulating sheath.

H7.43 IONIC COLLOIDAL CRYSTALS PRODUCED VIA CONTROLLED HETEROCOAGULATION. Gary R. Markosky, R. Edwin Garcia, W. Craig Carter, Yu-Ming Chiang, Massachusetts Institute of Technology, Dept. of Materials Science, Cambridge, MA.

Ionic colloidal crystals (ICCs) are here defined as ordered multicomponent colloids formed through heterocoagulation (electrostatic interactions). The conditions under which ICCs are stable have been analyzed. A model is presented in which two dimensionless parameters are found to fully characterize an ICC system. We calculate the Madelung constant of several ICC structures as a function of these two parameters, and discuss the parallels between the ICC Madelung constants and those for classical ionic crystals. Experimentally accessible regions of surface charge, salt concentration, and temperature where ionic crystallization could be possible are identified.

H7.44 AB INITIO STUDY OF THE ANODIZATION PROCESS OF CRYSTALLINE SILICON IN THE PRESENCE OF HF. Thompson Le Blanc, Daniel Melendez, Ivan Cao-Berg, Javier Avalos, Univ. Metropolitana, San Juan, PR.

Structures of nanometric porous silicon surface will be studied Ab INITIO using MP3 and BILYP basis sets, procedures which efficiently samples minima on a potential energy surface. This Scholastic procedure will try to model anodization process where the surface of the crystalline silicon becomes porous on the presence of HF. The most stable structures will be presented. It is shown so far that using the basis-set as described in the investigation, there was no change in the electronic density. In the future we will be using different basis-sets and smaller.
Kazuki Takashima and Yukihi Higo, Tokyo Inst of Technology, Tokyo, JAPAN.

Nano-sized crystals (NCs) have been intensively investigated in the past decade because of their excellent properties. Several methods have been proposed to obtain NCs, such as recrystallization following severe plastic deformation, epitaxial deposition, and 3D self-assembling. Electron-beam irradiation can grow then the NCs are irradiated with light or electron-beams. 1. P.W. Wu, et al., Adv. Mat. 12, 1488 (2000). 2. T. Deng, et al., An. Chem. 73, 645 (2000). 3. S. Stellacci, et al., Adv. Mat. 14, 194 (2002).

0:45 AM H8.3
FABRICATION OF PERFORATED FILM NANOSTRUCTURES.
A.L. Elias, K.D. Harris and M.J. Brett, Dept of Electrical and Computer Engineering, Univ of Alberta, Edmonton, CANADA.

We have demonstrated the fabrication of perforated thin films (PTFs), comprised of thin coatings perforated with uniform aperture shapes such as hexagonal or chevron. PTFs are fabricated using a template of nanopores or chevrons of diameter nominally 200 nm produced using the Glancing Angle Deposition (GLAD) technique. GLAD utilizes a combination of extreme oblique incidence physical vapour deposition with controlled substrate motion to engineer specific porous nanostructures. PTFs have been produced by filling template helical GLAD films with various substances, etching back the coating to reveal the tops of the helices, and etch removal of the helical template. We will report on a range of nanostructured materials fabricated using the PTF technique, including ordered periodic arrays of helical perforations, utilizing a template of arrays of nanopores. We are developing a process for fabricating micron PTFs, in which electropolishing is used to fill the original templates. We will also report on a replication process, using PTFs as a template, from which nanohelices can be fabricated in materials that cannot otherwise be used in the GLAD process, such as glasses.

0:15 AM H8.3

Conventional, broad-area, ion implantation through 3-d masks is of limited utility due to the presence of 3-d features, periodic in 2-d. Two examples are discussed. In the first, a self-assembled array of silica spheres is used as an implant mask. The lateral geometry of the spheres provides variable implantation depth in a periodic fashion. The ion beam amorphized regions of the substrate are then removed by selective chemical etching to achieve 2-d patterning. In the second example, self-assembled, nanometer-sized hole arrays are produced by electrochemical etching in aluminum. The porous aluminum films are then used as an implant mask to produce a periodic array of high aspect ratio, 40nm diameter holes on 100nm spacing in a single crystal substrate. We discuss the directions in which this type of lithography might be taken.

0:30 AM H8.4
3D MICRO- AND NANO-FABRICATION OF METAL NANOPARTICLE PATTERNS AND CONDUCTIVE METAL STRUCTURES VIA ONE- AND TWO-PHOTON INDUCED LITHOGRAPHIC AND HOLOGRAPHIC METHODS. Francesco Stellacci, Christina A. Bauer, Wim Wenseleers, Tim Meyer-Friese, Valérie Alain, Stephane M. Kuebler, Beth R. Mader, Joseph W. Ferry, Department of Chemistry, The University of Arizona, Tucson, AZ.

The photochemical generation of metal nanoparticles and metal structures in a solid matrix has recently attracted attention. We have shown that the use of a photoreducing dye that was designed to be chemically tunable to be used in a polymer matrix with a soluble salt (AgF2) allows for the photochemical generation of isolated silver nanoparticles. When the excitation is generated by use of interfering laser beams, the resulting refractive index contrast is sufficient for the one-step formation of very stable holographic images. The use of two-photon irradiation allows for the formation of 3D nanoparticle-containing patterns in a polymer matrix. We show that the enhanced fluorescence and/or the refractive index contrast, generated following exposure, can be used for 3D data storage. In order to obtain continuous metal features in a polymer matrix, pre-encapsulated metal crystals have been dissolved in the polymer matrix. Tailor-made ligand-coated metallic nanoparticles can be readily synthesized and can be made in complex composite materials or can be self-assembled and thermally annealed into ordered films. We have demonstrated that, in the presence of suitable reducing dyes and metal salts, it is possible to induce the growth of metal nanoparticles either under optical excitation or under electron-beam irradiation. We show further that it is possible to obtain continuous and conductive metal structures using optical excitation and that, with two-photon excitation, 3D self-assembling structures can be fabricated and characterized. Silver, copper, and gold microstructures will be presented. Finally, we will describe nanoparticles functionalized with covalently bonded dyes that can then be grown when the dyes are irradiated with light or electron-beams. 1. P.W. Wu, et al., Adv. Mat. 12, 1488 (2000). 2. T. Deng, et al., An. Chem. 73, 645 (2000). 3. S. Stellacci, et al., Adv. Mat. 14, 194 (2002).
that are ubiquitous to aquatic (marine and freshwater) environments. Distomas form intricate 3-D frustules (microshells) comprised of assemblies of silica frustules. Each kind of extant distom species is 10⁶ to 10⁷. Each species of distom forms a frustule with a unique shape and with fine, distinctive features (e.g., pores, ridges, protuberances). Continued reproduction of a given distom can yield large numbers (e.g., billions) of daughter distoms with a similarly-shaped frustules. Such massively parallel 3-D self-assembly of complex-shaped nanoparticle structures can be highly attractive for nanotechnology applications, however, the range of potential applications is limited by the silica-based chemistry of distom frustules. The compositional limitations of biotic-based structures can be overcome in the Bạc-Hc process through the use of shape-preserving fluid/solid reactions. This process has been demonstrated via the reactive conversion of two types of biologically-derived preforms: i) naturally-occurring distom frustules (e.g., capsule-shaped Anthocystis, disk-shaped Cyclotella), and ii) biocatalyzed multifilamento silica structures. The latter structures were produced through the use of silafins (baculata derived from distom). These preforms were converted to alkaline earth-bearing oxides (MgO-bearing or CaO-bearing) by exposure to elemental gases (Mg(g) or Ca(g)) at 2700°C. Electron microscopy (SEM, TEM) has revealed the preform shapes and fine features were preserved after conversion. Preform reactions to other ceramics are also under investigation. Such shape-preserving chemical conversion, coupled with future genetic tailoring, could ultimately yield a variety of Genetically-Engineered MesO/nanodevices (GEMs). U.S. Patent Application.

11:30 AM H8.9
NANOPARTICLE RIBBONS: A METHOD FOR FABRICATING COMPLEX 3-D ELECTRONIC CIRCUITS. Venugopal Santhanam, Ronald P. Andres, Purdue Univ., School of Chemical Engineering, West Lafayette, IN; B. Janes, Purdue Univ., School of Electrical and Computer Engineering, West Lafayette, IN; and Stephen W. Howell, Ronald Reifenberger, Purdue Univ., Dept. of Physics, West Lafayette.

The huge size mismatch between typical organic molecules and lithographically defined structures is a critical problem hindering implementation of "molecular electronics". One solution to this problem is to self-assemble circuits using nanometer-scale gold particles as conducting nodes physically linked and electrically coupled by organic molecules that have terminal thiol or disulfide groups (e.g. Science 273, 1690 (1996)). Researchers have been able to fabricate small monolayer arrays of such molecularly linked nanoparticles, but in order to construct functional devices and circuits, methods must be developed for fabricating lines or ribbons of linked nanoparticles and for assembling layers of these ribbons one on top of the other with selected organic molecules forming the interconnections between each layer. We describe a suite of techniques for construction of such 3-D nanoengineered assemblies: 1) a self-assembly method of forming a uniform, close-packed monolayer of alkane thiol-encapsulated gold nanoparticles spanning centimeters; 2) a soft lithographic method for transferring nanoparticle ribbons selected from the template; 3) a method for reshaping the alkane thiol molecules on the particles with conjugated diithiol molecules, which lower the lateral electrical resistance of the ribbons by three orders of magnitude; and finally a method for linking nanoparticle ribbons one on top of the other and forming defined molecular junctions between them. We characterize these 3-D nanoelectronic systems using Transmission Electron Microscope, and Kelvin Probe Microscope studies along with UV-Vis, and L-V measurements.

11:45 AM H8.10
3D NANOENGINEERING OF METAL OXIDES AND OXYHYDROXIDES FROM AQUEOUS SOLUTION. Lionel Vayssieres, Arumugam Manthiram, Texas Materials Institute, The University of Texas at Austin, Austin, TX

The ability to design anisotropic nanoparticles with tailored aspect ratio and to order them into large 3D array is an important challenge. Scientists have to face to create smart functionalized nanomaterials. One approach to control the size and shape of nanoparticles as well as the overall texture of nanomaterial thin films is to tune their direct aqueous hydrolysis-condensation growth onto substrates using the interfacial thermodynamics of nanocrystals as well as their kinetics of heteroconstriction. This is achieved by minimizing the surface energy at the Water/Oxide interface using a generalized quantitative model based on Gibbs adsorption equation. Indeed, growing materials at low interfacial tension, i.e., at thermodynamically stable conditions, allows to control elongation and rate of the nucleation stage and therefore different size, shape and orientations can be generated onto various substrates. Consequently, the design of novel devices with tailored and engineered three-dimensional architecture can be obtained without template or surfactant. Such ideas are static as demonstrated and illustrated on the design of nanorods and nanowires of zinc oxide, iron oxide and manganese oxide materials, their growth as 3D arrays with parallel and perpendicular orientation with respect to the substrate as well as the characterization of their electronic structure and opotlectric properties.

SESSION H9: APPLICATIONS OF FUNCTIONAL NANOSTRUCTURES

Chairs: Dhadi Meriak and David M. Taylor
Thursday, December 5, 2002 Room 309 (Hynes)

1:30 PM H9.1
ADVANCED CHEMICAL GAS SENSORS FOR OUTDOOR AIR QUALITY MONITORING. Maria-Isabella Barston, UMR CNRS 6098, Faculty of Sciences, Limoges, FRANCE

The popular Taguchi-type SnO2-based sensors are often used as low-cost alarm devices to monitor the indoor air quality. However they are not suitable for outdoor air quality monitoring due to their insufficient sensitivity to pollutant gases like CO, NO, NO2 and O3 at the sub-ppm level. I will review the results of two major research programs we undertook to optimize chemical gas sensors based on metal oxide semiconductors. Four major topics will be treated here: 1) how and why the use of nanopowders in the fabrication of screen-printed gas sensors leads to increased sensitivity. 2) how the printing of the sensitive layer on the alumina tiles using a simple mechanical layer-by-layer technique leads to further increase of the gas sensitivity, thus showing a beneficial effect of a 3D assembly of nanoparticles. 3) why the surface chemistry of nanoparticles is critical and must be tailored to optimize chemical gas sensors. 4) which of SnO2, In2O3 and WO3 nanopowders obtained by laser evaporation gives the best sensitivity to CO, NOx and O3 in presence of humidity. The prototype devices which could detect SO2 and NOx concentrations down to 20 ppb and 50 ppb respectively, and CO concentrations down to 3ppm in air were characterized by various methods including XRD, TEM, FTIR, and electrical measurements. The SMOGLES and INTAIRNET projects were financially supported by the European Community (contracts numbers BRPR-Ct96-0062, and IST-12615).

2:00 PM H9.2
CHARACTERIZATION OF NANOSIZED TIN-OXIDE NANO PARTICLES FOR FABRICATION OF A HIGH SELECTIVITY MICRO GAS SENSOR. R.C. Ghan, Y. Lvov, R.S. Beaser, Institute for Micromanufacturing and Chemical Engineering, Louisiana Tech University, Ruston, LA

We are investigating properties of SnO2 nanoparticles deposited using a novel Layer-by-Layer (LbL) technique in order to develop high selectivity, nanostructured, semiconductor micro gas sensor. While SnO2 for gas sensing is not new, the advantages of the LbL process give promise for a new class of devices. Nanoparticles were synthesized from readily available nanoparticle building blocks. As presented in the 5th Fall Meeting, Boston, 2001, we have achieved precision SnO2 nanoparticle deposition on QCM resonators. Subsequently, we have used the self-assembly technique [1]. Besides SnO2 films, films of SnO2/SnO2 were alternately assembled with a view to investigating doping effects. SEM characterization of as-deposited films show that the SnO2 nanoparticles thin films are grown uniformly across the substrate. The size range for the nanoparticles is 3-5 nm. Electrical characterization of newly prepared macro-scale prototypes reveals linear current-voltage characteristics indicating ohmic behavior. An issue in the use of the LbL process is the presence in the film of residual organic residuals from the growth process. Calculation experiments show significant residue, even after 500°C. This is a matter of concern since the use of higher temperatures begins to diminish the basic advantages of the LbL process over conventional ceramical processes. We will present the results of these studies, and others for removing residual polymer components. We will also show the results of an alternative approach for preserving the electrical activity of the SnO2 oxide nanoparticles while maintaining lower processing temperatures. References [1] R.C. Ghan, Y. Lvo, R.S. Beaser, "Characterization of Self-Assembled Tin-Oxide Films for High Sensitivity Micro-Gas Sensors," MRS Proceedings, Materials Research Society, College Park, MD, 2001.

2:15 PM H9.3
NANOMECHANICAL SYSTEMS. H.G. Craighead, Applied and Engineering Physics, Cornell University, Ithaca, NY.

We have created mechanical devices, using a variety of materials, that we have been studying as sensors and other applications. In most cases the motion of these devices was detected and in some cases
acted by the application of light. Spatially varying mechanical driving of micromechanical structures was also demonstrated using a scanning piezo actuation and a focused laser beam to drive motion. Sensor applications include immunospecific detection of single bacterial cells and chemical monolayers. Parametric amplification of mechanical resonance was demonstrated with dimensions down to tens of nanometers. The smaller devices are also more susceptible to surface related mechanical loss mechanisms, which we have begun to study. Related nanofabrication approaches have also been used to create micromechanical systems for the mechanical manipulation and sorting of molecules by mechanical and physical properties in a variety of fluid containing system configurations. Mechanical confinement of molecules has also been used to enable optical detection and analysis of individual biomolecules.

2:45 PM **H.P.**

**OPTICALLY Driven MICROMANIPULATION TOOLS**
**FABRICATED BY TWO-PHOTON MICROSTEREOLITHOGRAPHY.**
Shoji Maruo, Koji Ikuta and Masato Korogi, Department of Micro System Engineering, School of Engineering, Nagoya University, Aichi, JAPAN.

Manipulation techniques at micro and nanometer length scale are crucial for advance in biotechnology as well as nano science and technology. Several types of nanomanipulators such as carbon nanotube nanowebers and micromachined nanowebers have been developed for grabbing or probing micro/nano scale objects. However, manipulators are based on electrostatic force, they are not ideal for aqueous solution work such as manipulation of cells, microbes and single molecules. In this paper, we report optically driven micromanipulation systems suitable for biological applications that require work in aqueous solution. Our manipulators were fabricated by using two-photon microstereolithography [1,2]. These micromanipulators are controlled by optical trapping based on radiation pressure from a tightly focused laser beam. Since optical trapping enables remote driving of movable micromechanisms in biological fluid environments, the micromanipulators are well suited for the application in biotechnology. The main advantages of our optically driven manipulators are as follows: 1) Remote drive suitable for aqueous solution work, 2) Femtosecond laser control, and 3) Easy integration into micro total analysis systems. We fabricated micromanipulators whose arms is 8.7 mm long and 1.7 mm wide. By trapping and swinging a manipulator arm with a focused laser beam, the micromanipulators were successfully opened and shut in a liquid. In addition, we succeeded to control the torque of the manipulators by adjusting the position trapped by the laser beam along the length of the arm. The range of the torque was on the order of 10^-12 Nm. Finally, we developed microwebers and microwebers with probe tips of diameter 250 nm. These manipulators were also driven in a liquid. Such optically driven micro/nano manipulators are promising tools for biotechnology and micro total analysis system.


3:30 PM **H.D.**

**BIOLOGY DOES IT DIFFERENTLY. HOW CAN WE HARNESS ITS ADVANTAGES?** Daniel E. Morse, Jon Sunmer, Wenjun Yang, Timothy F. Deming, Bradley F. Chmelka, Gaten D. Stucky and Paul K. Hansma, University of California at Santa Barbara, Biomedical Science and Engineering and Materials Research Laboratory, Santa Barbara, CA.

Biological systems fabricate 3-dimensional nanostructured composites by mechanisms that are both more precise than, and fundamentally different from, those of current technologies. Two examples are discussed. (1) Whereas multi-layer spin-coating, dipping or stencilled vapor deposition strategies are used in current manufacturing technologies to produce multi-layered structures for microelectronics, the biological mechanism underlying formation of the microcrystalline mineral-organic composite forming the nacre of pearls and seashells is fundamentally different. Microcrystalline nacre is organized over macroscopic dimensions by continuous growth of atomically coherent aragonite crystals propagating from one layer to the next through nanofibers in a layered network of sheets composed of a fabric of proteins and polysaccharides. Stochastic spacing of the aragonite nanowires and the interval between successive microcrystals, thus generating the interdigitating brickwork of crystalline plates that contributes to enhanced fracture toughness. While this mechanism generates the hierarchically organized multilaminar pattern, families of small proteins interact stereospecifically with the growing crystals to control their polymorph, atomic structure orientation and morphology. (2) The intricate structures of silica produced biologically in sponges in diatoms similarly reflect the continual operation of multiple mechanisms operating contemporaneously at different length scales. In sponges, for example, the formation and deposition of silica is catalyzed and nanostructurally directed from the bottom up, in contrast to differential lithographic and etching techniques) by a unique family of enzymes that simultaneously provide the catalytic centers for the formation of silica while at the same time providing the templates for its deposition. Higher-order structural control is thought to result from phase-separation operating in conjunction with molding by the surrounding lipid membranes. Higher-order branching of silica spines reflects the controlled branching of the structure-directing proteins on which the silica is deposited, but understanding the regulation of this branching at the protein (catalytic template) level presents a significant challenge. Progress in biomimetic adaptation of these mechanisms - including methods now in use by specialized sectors of the semiconductor industry - will be discussed.

4:00 PM **H.G.**

**FABRICATION OF 3-D BIOACTIVE STRUCTURES.** Kenneth E. Gonsalves, Dept. of Chemistry & C.C. Cameron, Applied Research Center, Univ. of North Carolina, Charlotte, NC; Wei He, Dept. of Chemistry, Univ. of Connecticut, Storrs, CT; Ashutosh Chilkoti, Dept. of Biomedical Engineering, Duke University, Durham, NC.

Three-dimensional micro- and nanostructures have significant potential for biomedical applications. In our studies, various approaches have been applied for forming the components of the approach uses masked ion beam lithography (MIBL), which simultaneously modifies both the surface topography and chemistry. Spin coated PMMA films were submitted to ion implantation. Arrays of holes with nanoscale depth and microscale width were generated, and surface hydrophobicity was modified during the process. The effect of ion implantation on cell attachment was evaluated by culturing osteoblast cells on the substrates. The other approach used UV polymerization to fabricate patterns. The bottom layer of the structures would be custom-designed bearing adhesion-promoting peptides or growth factors. The surface was patterned with various monomers by irradiating UV through a projection mask. A structure consisting of a nonfibrous surface with bioactive channels was achieved. It is also possible to build multiple layers through this technique. Alignment of fibroblast cells and extracellular matrix formation is the final objective. In a modified approach, we have shown that an amphiphilic comb polymer film with short oligoethylene glycol side chains appended on a MMA backbone can be used as a physico-chemical barrier to prevent cells on substrates. Microcontact printing the comb polymer on a substrate and then backfilling the unpatterned regions of the substrate with a cell adhesive protein fibronectin (FN), or vice versa, created highly resolved micropatterns of cells in 10% serum for up to a month in culture. AFM of the microstamped surfaces indicated 3D like nanostructures. All these methods might provide routes to control the interaction of cells with diverse substrates for applications in biomaterials and biotechnology.

4:30 PM **H.H.**

**BIO-INSPIRED SELF ASSEMBLY OF MICRO- AND NANO-STRUCTURES FOR SENSING AND ELECTRONIC APPLICATION.**
H. McNally, S.W. Lee, D. Guo, M. Pingle, D. Bergstrom, R. Bisbak\*; School of Electrical and Computer Engineering, Department of Medicinal Chemistry, Department of Biomedical Engineering, Purdue University, W. Lafayette, IN.

Bio-inspired assembly, through the use of bio-molecules such as DNA and proteins, will play a critical role in the advancement of novel biosensing techniques and for the realization of heterogeneous integration of materials. For many of these applications, such as antibody-based biosensor and the study of controlled cell growth, DNA and protein patterning techniques are crucial. We will present an update of our work on protein patterning techniques using microelectronic fabrication, DNA hybridization and protein-activating pairing. Fluorescein conjugated streptavidin and Anti-Listeria Antibodies were patterned as a demonstration. To show its application in biological inspired self-assembly, this technique was used successfully in the self-assembly of 20 nm streptavidin conjugated gold particles. In addition, the integration of nano- and micro-scale heterogeneous materials is very important for novel material synthesis and electro-optic applications. We will present an update on our work to assemble silicon electronic devices using DNA/charged molecules and electric fields. Device are fabricated, released, charged with molecules, and subsequently manipulated in electric fields. Electrical properties of these devices including resistors and junction diodes are investigated after the assembly has occurred. The techniques described can be used to integrate the hybrid device such as nano- or micro-scale resistors, PN diodes, and MOSFETs on silicon or other substrates such as glass, plastic, etc.