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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 Blaike (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 Goesele'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 Loeschnner (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 McIlroy'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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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 to ensure the industrial viability of nanotechnology is the selection of a 3D nanofabrication method that can be scaled up. This tutorial will describe state-of-the-art lithographic and non-lithographic methods and critically compare their performances in fields as diverse as 3D nanofabrication, photonic crystals, and electronic devices.

Instructors:
Shinji Matsui, Himeji Institute of Technology
John A. Rogers, Bell Laboratories, Lucent Technologies

SESSION III: NANOFABRICATION VIA LITHOGRAPHIC TECHNIQUES
Chairpersons: USD 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.R.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 ~75 nm are possible. Since the limitation in optics is on the period rather than the linewidth, nonlinear interpolation techniques allow extensions to ~37 nm and below. Integration of the periodic IL and non-lithographic methods and optical lithography to provide isolated areas of nanofabrica does offer a powerful patterning capability with application in many areas including nanofabricated crystal growth, photonic crystals, magnetic materials, molecular electronics and nanostructure-biology interactions. Particular emphasis will be placed on the use of nanofabricated substrates for semiconductor crystal growth. Examples will be drawn from MOCVD nanoheteroepitaxy growth of engineered quantum wires and dots in the InAs/GaAs system.

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 directly onto non-planar (e.g. rough, curved or multi-levelled) surfaces. This talk describes some of these methods and it gives examples of their use in electronics, photonics and certain areas of biotechnology. In particular, we illustrate how microcontact printing onto cylindrical supports can yield (i) microsprockets for MEMS, (ii) conducting microcoils for inductors, transformers and excitation/detection coils for high resolution NMR, and (iii) free-standing metallic microstructures for intravascular stents. This printing approach and a related method for nanomolding also provide direct routes to three dimensional nanostructures (e.g. distributed feedback gratings on the top surfaces of rib waveguides) that are useful as components in integrated optical systems. Finally, we introduce a nanotransfer printing technique that is capable of purely additive, single-step patterning of complex multilayer stacks with near-molecular edge resolution. We illustrate some applications of this method in plastic and electronic electronics.

9:30 AM • H1.3
ION PROJECTION DIRECT-STRUCTURING (IPDS) FOR NANOTECHNOLOGY APPLICATIONS. Hans Loescher, Elmar Pitzgruber, and Gerhard Stengl, IMS Nanofabrication GmbH, Vienna, AUSTRIA.


Proton Beam Micromachining (PBM) using MeV protons has the unique capability of producing direct-write high-aspect-ratio 3D structures in resist material. Protons, being 1860 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 into 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 microphotonicics, microfluidics, tissue engineering substrates, and is also particularly suited to the rapid production of high quality 3D stamps and molds for soft lithography using polymers. In addition, recent advances in quadrupole 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 • H1.4
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 in 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 calixarenes, to choose from to achieve high resolution in electron-beam lithography. However, these materials suffer from the limitation of poor 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 describe 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 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. Lau, Y. Zhu, Brookhaven National Laboratory, Upton, NY.

A goal of this project is to tailor assemblies of Co/CoO structures for the purpose of studying magnetic behavior between 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 aluminum fluoride film was subsequently deposited as a 200 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 limits of CA and conventional materials in terms of shot-noise and resolution limits in terms of e-beam solid interactions.
We present new results in the generation of chemical nanostructures on aromatic self-assembled monolayers. Using electron beams, biphenyl and silicon are cross-linked on the nanometer scale while reducible terminal groups such as nitro or cyano are locally reduced to amino functionalities. Additional on aromatic self-assembled monolayers. Using electron beams, Physikalisch-Technische Bundesanstalt, Braunschweig, GERMANY. Universitat Heidelberg, GERMANY; Thomas Weimann, Peter Hinze, We present new results in the generation of chemical nanostructures nm are generated. Alternatively, the patterns can be transferred into the substrate by chemical etching techniques, such as metal nanostructures, 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 nanostructures that sets up coupled plasmon modes of the nanostructured arrays. This coupling leads to coherent propagation of energy along nanoparticle and nanorod arrays whose group velocities are greater than the speed of light, and can be guided around 90 degree corners and split via tee structures with high efficiency. We have confirmed our theoretical predictions in a macroscopic analog operating in the microwave region with via experiment, full field electrodynamic 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 nanostructures in a variety of geometries such as parallel, corner and tee structures using electron beam lithography on ITO coated glass substrates and assembly using atomic force microscopy or evanescent lithography. 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 16 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.

SESSION H2: PLASMON PROCESSES ON THE NANOSCALE
Chairs: 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 NANOMETER 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 itself 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 (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 (God given) characteristic length scale? Naturally, its property will change, and equally important, becomes sensitive to its size or shape. Thus each material can, in principle, has multitudes 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 upon changing their shape. The properties studied are, the optical and nonradiative properties, the femtosecond electron dynamics in semiconductor nanoparticles, and the ultrafast photothermal shape changes of gold nanorods to spheres.


2:00 PM *H2.2
TAILORING NANOPARTICLES WITH LASER LIGHT.
Frank Wagner, Universitat Kassel, Kassel, GERMANY.

The physical and chemical properties of nanoparticles or, more generally, small 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 to generate, control and manipulate metal nanoparticles 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 distributions 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, prospects and applications will be outlined.

3:00 PM *H2.3
SUBWAVELENGTH SCALE PHOTONIC STRUCTURES.
Harry A. Atwater, Stefan A. Majer, 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 skinned 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 nanostripes, 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 nanostructures that sets up coupled plasmon modes of the nanostructured arrays. This coupling leads to coherent propagation of energy along nanoparticle and nanorod arrays whose group velocities are greater than the speed of light, and can be guided around 90 degree corners and split via tee structures with high efficiency. We have confirmed our theoretical predictions in a macroscopic analog operating in the microwave region with via experiment, full field electrodynamic 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 nanostructures in a variety of geometries such as parallel, corner and tee structures using electron beam lithography on ITO coated glass substrates and assembly using atomic force microscopy or evanescent lithography. 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 16 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 NANOLITHOGRAPHY USING EVANESCENT FIELDS.
Richard Blaikie, Manu Allouis, 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 possibility of using optical/nanolithography without the need to use expensive, deep ultraviolet light sources [1]. We have been studying photolithography techniques that utilize 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 using evanescent fields will be explored. It is found that the exposure wavelength is of secondary importance in this regime, and that the properties of the mask are much more significant. Scaling to smaller feature sizes requires the better 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 principle of applying negative refraction and surface plasmons to improve the resolution in the evanescent near field will be described. 1. Almassi, et al., Appl. Phys. Lett. 77, 3560 (1999); 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.
Andrew L. Martin, Pieter G. Kik, Stefan A. Majer, 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 50 nm using conventional photore sistors.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 produces a strongly enhanced 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 40nm Ag sphere using p-polarized 435nm light directly incident on the sample is 30-80 nm in diameter (0.65) 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 photore sist. We also explored the importance of the medium above and below the resist layer and the angle of incidence. Printing experiments using 40nm diameter silver colloid deposited directly onto the 55-75 nm thick g-line resist layers on FIB 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 nanoscale depressions in exposed resist layers, providing evidence for plasmon-enhanced resist exposure. We will discuss 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 Molecular Self Assembly to Biotecnology (Mat. Res. Soc. Proc., Boston 2001).

**4:15 PM H2.6**

**THE CONSTRUCTION OF SPHERICAL ASSEMBLIES BY GOLD NANOPARTICLES MEDIATED WITH MULTI-DENTATE THIOETHER LIGANDS.** Matthew M. Mayo, 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 and organic ligands promise interesting technological applications in sensors, catalysis, drug delivery, microelectronics and medical diagnostics. However, the ability to assemble them with controllable dimensions and spatial properties is still very limited. This presentation describes novel findings of the assembly of gold nanoparticles via multidentate organosulfur molecules. Two different ligands are used: 1) Thiacrown derivatives and 2) mercaptoalkylphosphonates. The use of polymers as stabilizing agents for the controlled synthesis of metal nanoclusters.

**4:30 PM H2.7**

**DIRECTED SELF-ASSEMBLY OF ORDERED METAL NANOCLUSTERS USING A FOCUSED ION BEAM MICROSCOPE (FIB).** M.D. McMahon, A.B. Hmelo, R. Lopez, R.F. Haglund Jr., L.C. Feldman, Dept. of Physics and Astronomy, Vanderbilt University, Nashville, TN; R.A. Weiler, Dept. of Electrical Engineering and Computer Science, 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 spatial arrangement of individual nanocrystals. Ordered arrays of metal nanoparticles have potential applications as elements of nonlinear optical devices, as sensitizers for fluorescence emission and photodetectors, and as sensors for fluorescence imaging. The optical response of an ensemble of nanoparticles is the sum of the response of individual nanoparticles. Our approach to promote the formation of ordered metal nanocrystal arrays for optical investigations is to explore the following technique: 1) Fabrication of ordered arrays of gold nanocrystals on FIB-processed substrates using repulsive deposition and 2) Fabrication of ordered arrays of silver nanocrystals on surfaces by focused ion beam (FIB) deposition. The results demonstrate the feasibility of using focused ion beam (FIB) deposition to fabricate ordered arrays of metal 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.** Meg Abraham, Oxford University, Dept of Materials, Oxford, UNITED KINGDOM.

Photo-writeable glass is a commercially available material that can be patterned using a standard UV photon exposure and bake process. It has been demonstrated for the first time how plasmons or free conduction band electrons in metallic nanoparticles on glassy glassy matrix that can form nano-crystalline nucleation sites and eventually small SiO2 or metal crystals when annealed at higher temperatures. To date the use of photo-writeable 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 nucleation 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: NONLITHOGRAPHIC TECHNIQUES**

**Tuesday Morning, December 3, 2002**

**Room 309 (Hynes)**

**9:00 AM H3.1**

**SHAPE VARIATIONS AND CONTROL IN SELF-ASSEMBLED METAL NANOCLUSTERS.** Rita Tannenbaum, 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 adsorption of polymers to distinct crystallographic faces of the growing metallic fragments, caused 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 nanoparticle shape. For example, in the presence of poly(vinylidene difluoride) (PVDF), the thermal treatment of a metal carbonyl-polymer solution in alcohol and polymer film formation ("hot" method), gives rise to nanopyramids. 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 nanostrings 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 to the effectiveness of the capping process by the adsorbed polymer layer.

**9:45 AM H3.2**

**SELF-ASSEMBLED HIERARCHICAL-STRUCTURES OF EMULSIONS AND FINE PARTICLES.** Sachiko I. Matsushita, RIKEN Frontier Research System, Frontier Hierachy Structures Lab, Saitama, JAPAN; Nobuhito Kuroko, Masatsugu Shimomura, 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 microscale 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 Prigogine won the noble prize in 1977, dissipative process is well known and it is potentially of great scientific and technological interest because the process is simple, self-assembly, inexpensive system to prepare wide-range architecture, from nanometer to microstructure. Especially, one of the important points of dissipative process is capability to make hierarchy structures that will birth diversity and complexity, as every creature does. Among many dynamic processes such as dissipative structures, we attracted honeycomb-like structures. This honeycomb-like structure can be formed in a volatilized process of polymer suspensions by exposure in humidity air, and the final structure has hexagonally hole-packed air-spheres (0.2 - 10 µm diameter) like a comb of honeybees. Possible applications of such honeycomb structures itself include membranes for separate, microreactors, bio-interfaces, 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-like structures. As the results, a periodic hierarchically array composed of microporous polymer micelles and submicron fine polystyrene particles, variously dispersed mixtures of metal clusters and polymer are of interest both for synthesis, and all have their limitations. In our laboratory, we have developed a way to produce clusters or 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 vapor-deposition of the two components. Production of homogeneous distributed nanoclusters with narrow size distribution embedded in polymer matrices is accomplished. Tandem evaporation method particularly demonstrates that the cluster size and distribution can be controlled independently with cluster volume filling. Some of the optical and magnetic properties of the prepared composites are also discussed.

9:45 AM H3.3
VAPOR PHASE DEPOSITED NANOCOMPOSITES OF POLYMER CONTAINING THREE DIMENSIONALLY DISPERSED METAL CLUSTERS.
Franziska J. Kanzow, J. Kanzow, J. Zapparicheskos, G. Strunkusk and F. Faupel, Lehrstuhl für Materialverbunde, Technische Fakultät der CAU, Kiel, GERMANY. 1Lehrstuhl für Physikalische Chemie I, Ruhr-Universität, Bochum, GERMANY.

Nanocomposites two component materials consisting of finely dispersed mixtures of metal clusters and polymer are of interest both from the fundamental and technological aspects in terms of several new nanomaterial properties. The microstructure and many physical properties of such composites depend on the method of preparation. A completely new technique vapor phase thermal evaporation is employed to prepare nanocomposites of polymer containing metal clusters. Nanocomposites of three dimensionally dispersed clusters (Ni, Au, Cu) in various polymer matrices (Teflon AF, PI) are fabicated by following co-evaporation to tandem deposition in the form of many sequential evaporation of the two components. Production of homogeneous distributed nanoclusters with narrow size distribution embedded in polymer matrices is accomplished. Tandem evaporation method particularly demonstrates that the cluster size and distribution can be controlled independently with cluster volume filling. Some of the optical and magnetic properties of the prepared composites are also discussed.

10:00 AM H3.4
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 a way to produce clusters or 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 vapor-deposition of the two components. Production of homogeneous distributed nanoclusters with narrow size distribution embedded in polymer matrices is accomplished. Tandem evaporation method particularly demonstrates that the cluster size and distribution can be controlled independently with cluster volume filling. Some of the optical and magnetic properties of the prepared composites are also discussed.
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 change over the last decade. Much of the Oil and Petrochemicals industry production has shifted irrevocably 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 nanoscalar and nanostructured materials generation. In this talk I will try to give a view of some of the 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 from a fluid phase which can be a simple single component system 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 Nanoscalar 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 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 nm for bulk storage and flow to 1 nm for desirably aggregated primary particles to 1-10 nm for “quantum dot” type nanochannels which exhibit spectacular changes in luminescence for example. I will illustrate the above with examples of nanoscalar synthesis and assembly processing technologies which deliver extreme effects and functionality.

SESSION H4: FABRICATION AND PROPERTIES OF 2D-ORDERED NANOSTRUCTURES
Chair: Koji Ikuta and Lhadi Merhari
Tuesday Afternoon, December 3, 2002
Room 309 (Hynes)

1:00 PM *H4.1
TWO-DIMENSIONAL ORDERED NANO PORE ARRAYS: FABRICATION AND FILLING WITH MATERIALS. Ulrich Goesele, Ralf Wehrspohn, Jinsub Choi, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

We have investigated two-dimensional ordered pore arrays and their filling with metal wafers such as various metals on the basis of two different material systems. One material system involves pores in silicon, the other one pore arrays in aluminum oxide fabricated by anodic oxidation of silicone. 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 metal wafers with varying diameter. This technology 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 nanowires 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
3D NANOSTRUCTURE FABRICATION BY NANOIMPRINT LITHOGRAPHY & LITHOGRAPHICALLY INDUCED SELF-ASSEMBLY. Paru Deshpande, \textit{et al.}

As semiconductor devices continue to shrink, low-cost, large area, 3D nanoimprinting is becoming increasingly significant. Such 3D nanoimprinting 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 nano fabrication that can be extended to three-dimensional structures. The first, nanoimprint lithography (NIL), is a low cost, high throughput nano-patternning process in which a mold is used to locally 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 between the substrate and mask. Furthermore, the pillars can be aligned to patterns in the mask allowing for precise control of the position and crystal structure of the pillar array. Such structures can be used as scaffolds for 3D architectures or as features on top of pre-existing patterns.


3:30 PM H4.4
SELF-ASSEMBLY OF NANOSHEETS USING MAGNETIC FIELD. Jean-Christophe P. Gabriel, Franck Camaret, Patrick Batail, Sciences Moléculaires aux Interfaces, CNRS, Nantes, FRANCE; Bruno J. Lemaire, Patrick Davidson, Lab Physique des Solides, CNRS, Orsay Univ, FRANCE; Hervé Desvaut, 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 nanosheets can be tuned from 1 nm to 50 nm by strongly 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, $\beta$-SHEET-DERIVED PEPTIDE. Nathan Lockwood, Univ of Minnesota, Dept of Chemical Engineering and Materials Science; Robert van Wagenen, Kevin Mayo, Univ of Minnesota, Dept of Biochemistry, Minneapolis, MN.

We observed gelation of a 23-residue peptide derived from the $\beta$-sheet domain of platelet factor-4 (PF424-46). Optical and electron microscopy revealed gels composed of heterogeneous mixtures of 50 to 200 nm spherical aggregates in a less-dense gel matrix. Infrared and circular dichroism spectroscopies showed that gelation involved the conversion of PF424-46 from an unstructured, random coil state to an extended $\beta$-sheet conformation. We used aggregation-induced NMR peak intensity decay to show that temperature, pH, and ionic strength influenced PF424-46 gelation rates. Under identical solution conditions, gel formation took days at $T < 50^\circ C$, but only 30 minutes at $T \geq 50^\circ C$. Gelation was most rapid at pH values near the pKa of His35, the central residue of the peptide. Increases in solution ionic strength reduced the critical gelation concentration of PF424-46. The results of our study share characteristic of self-assembling peptides reported by other groups. Based on our results, we pose a hypothetical
model of PF_4− and 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-METAL PARTICLES IN AMORPHOUS CARBON FILMS
Gerhards, H., Hofstätter, and C. Ronning, II. Physikalisches Institut; H. Gibhardt, Institut für Physikalische Chemie; M. Seibt, 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, or the potential use for high density recording media. This motivated our study on the formation of metal nano-particles in amorphous carbon thin films (a-C:Me, Me = Cu, Ag, and Fe) prepared by mass selected ion beam deposition (MSIBD). Cu, Ag, and Fe have been characterized using X-ray photoelectron spectroscopy (XPS), Rutherford backscattering (RBS), Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). EELS were grown with varying metal to carbon ratios at room temperature on silicon substrates by co-deposition of low energy carbon and metal ions. The carbon matrix proves to be diamond-like with a high sp3-bonding content at low metal concentrations and becomes more graphitic with increasing metal content. Copper forms nano-particles within the matrix due to the vanishing solubility in carbon. The sites 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. Rousset, Peter T. Lellehøi, Emilie J. Siethövel, ICASE; Advanced Materials and Processing Branch, NASA-Langley Research Center, Hampton, VA.

The use of molecular interactions to assemble polymer/single walled carbon nanotube (SWNT) films will be discussed. Using a utilized groups present on carbon nanotubes, films have been formed via the repetitive electrostatic adsorption of carbon nanotubes onto surfaces treated with a positively charged polymer. Films prepared by this sequential adsorption method displayed linear growth characteristics as monitored by absorption spectrophotometry. Both probe and electron microscopy of these films revealed that films could be prepared which contain a very high concentration of SWNTs. The use of a bottom-up approach to assemble polymer/SWNT composite films allows a targeted level of control over film characteristics. We will demonstrate that by varying the adsorption conditions, one can tailor the amount, orientation, and vertical placement of the SWNTs within the film.

4:30 PM H4.8
SELF-ORGANIZED ZnO NANOISLANDS WITH LOW-DIMENSIONAL CHARACTERISTICS ON SiO_2/Si SUBSTRATES BY METALORGANIC CHEMICAL VAPOR DEPOSITION
Sang-Woo Kim, Shigeo Fujita, Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN; Shinsu 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 excitonic effects promise for achieving large oscillator strength, nonlinear optical properties, or multie exciton 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 SiO_2/Si substrates by metalorganic chemical vapor deposition by introducing either N_2O or NO gas as an oxygen source and diethylzinc as a zinc source on thermally grown SiO_2 films. Reactive N_2O gas was used as an oxygen source was found to be 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 14 nm and the density in the order of 10^{16} cm^{-2} could be obtained. More recent study is effectively going on to decrease the size and increase the density. In microscopic photoluminescence measurements at 10 K using a 325 nm He-Cd 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.

4:45 PM H4.9
MORPHOLOGY EVOLUTION OF PYRAMID-LIKE NANOSTRUCTURES ON COBALT THIN FILMS DURING DEPOSITION BY SPATTERING
Shih-Wei Chen, Jin-Ruey Wen, Chuan-Pu Liu, Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, TAIWAN; Juan-Nan Chen, Department of Electrical Engineering, Fortune Institute of Technology, Kaohsiung, TAIWAN.

The cobalt thin films are grown by D.C. magnetron sputtering as a function of the target-to-substrate distance, bias and power. The electrical properties, crystal structure and morphology of the thin films are characterized by 4-point probe, x-ray diffraction, scanning electron microscopy, transmission electron microscopy and atomic force microscopy. It is found that the cobalt crystal structure can be varied from FCC to BCC by varying the target-to-substrate distance from 6 to 10 cm. The resistivity, roughness and the preferred orientation of the thin films are greatly affected by the substrate bias and power. The lowest resistivity of Co films is 9.8 μΩ-cm when deposited at the target-to-substrate distance of 6cm, the applied power of 50W and substrate bias of -75 volts. In addition, pyramid-like nanostructures with sharp tips are formed on the surface of the thin films when negative bias is applied. The faceted planes on the nanostructures depend on the resulting Co crystal structure while the size and density are determined by the growth parameters. The evolution of the surface nanostructures are systematically examined as a function of bias substrate and thin film thickness. The formation mechanism of the surface nanostructures is discussed in the paper.

SESSION H5: FABRICATION AND PROPERTIES OF NANOWIRES, NANORODS AND NANOTUBES
Chairs: Koji Ikuta and Thomas Orlando
Wednesday Morning, December 4, 2002
Room 305 (Hynes)

8:50 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 (50-200 nm in diameter and 1-6 microns in length). These studies have provided us with strategies to attain two-dimensional and three-dimensional assemblies of nanowires. Typically, an nanoteel is derived with SAM 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. Ratt-like structures may be obtained by employing lithographically patterned substrates. Microcontact printing has been used to pattern surfaces with a variety of SAM forming molecules whose domains are commensurate with the rod dimensions. 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 NANOSPINDLES: UNEXPECTED CATALYST MEDIATED GROWTH PHENOMENA
David N. Mcllroy, D. Zhang, A. Alkhateeb, 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 catalytic phase, 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 film synthesis. Recently not only has the effects of the catalyst dynamics on nanowire geometry been realized, but the role of the catalyst also depends on the appropriate conditions for the growth of nanowires, or nanospindles, can be
achieved. The prerequisites for nanospring formation are as follows: (1) The composition of the nanowire forming the nanospring must be amorphous, (2) the catalyst diameter must exceed that of the nanowire forming the nanospring. To date, boron carbide nanosprings have been realized, however, the route towards determining the composition of the nanowires or nanosprings. 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 H5.3 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, Dept 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 conductive properties of carbon nanotubes. 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 factors such as the alignment, concentration, surface treatment, type and dispersion of nanotubes in these composites, 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 nanoporous composite films, in addition to reducing their electrical and ionic resistance. Consequently, electrochemical capacitances in excess of 2.0 F/cm² were obtained for the composite films with ratios 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, nanostructured semiconductors are expected to show distinctive optical and electronic properties from bulk materials. A number of nanocrystalline structures, such as carbon nanotubes and semiconductor nanowires, have been fabricated and studied. In this work, both the electronic and electrical properties of carbon nanotubes and nanowires with controlled structural configurations, their electronic and optical properties are still debatable. Here we report the study of the electron field emission and light emission of carbon nanotubes and CdS nanowires. Carbon nanotubes used for this study were synthesized directly on the surface of tungsten or silicon substrates. 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 (CH₂) 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-liquid-solid (VLS) mechanism. The diameter, length, and growth directions of the nanowires and nanotubes 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 ~1 x 10⁻⁸ Torr) equipped with a Faraday cup and a spectrum analyzer. The measurement suggests that the theoretical model of nanotube emission behavior while at higher applied fields, current saturation appears to be determined by the stability of the catalyst was used to characterize the current fluctuations observed in the Faraday cup current. Power spectral densities with regions following various (1/f)γ 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 was increased from 3100 V to 3700 V. The electron and light emission mechanisms of nanotubes and CdS nanowires will be discussed.

10:30 AM H5.5 GRAPHITE-BASED ELECTRONICS. Claire Berger, Yan Yi, and Walter A. de Heer, School of Physics, Georgia Institute of Technology, Atlanta, GA.

Carbon nanotubes are currently actively investigated for their electronic applications potential. We have recently found that carbon nanotubes are ballistic conductors at room temperature with mean free paths exceeding 50 nm. Nanotubes found to be semiconductors or metals depending on their geometry and doping and innovative transistor prototypes have been demonstrated. These advances show that nanotubes may indeed have applications 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 in which function as active circuits. We also present recent attempts to lithographic pattern graphite in order to realize active nanographics devices.

11:00 AM H5.6 GRAPHITE NANO TUBES: NEW FAMILIES OF CARBON NANO TUBES. Vitor R. Coluci, Scholla P. Braga, Sergio B. Legoa, 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 structural alternative for conventional carbon nanotubes (CNTs). One example of these forms is graphyne, an allotrope of carbon consisting of planar molecular sheets containing only sp² and sp³ 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 graphyne motifs. In analogy with carbon nanotubes, these graphyne tubes would be formed rolling up graphyne sheets to form seamless cylinders. Electronic and structural properties were analyzed using tight-binding and ab initio density functional methods. Our results show that these graphyne tubes present richer structural and electronic properties than conventional nanotubes. The high porosity in the graphyne nanotubes shells 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 BNC NANOTUBES. Vincent Meunier, Thomas Zacharia, Oak Ridge National Laboratory, Oak Ridge, TN, Christopher Roland, J. Bergholt, 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) nitride (N) nanotubes or BNC 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 COTs 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 H5.8 METAL NANOWIRES ARRAYS FOR CHEMICAL SENSING.
A general method is described for the preparation of arrays of metal nanowires. Nanowires composed of noble or coinage metals including copper, nickel, gold, palladium and other metals with diameters in the range from 60 nm to 750 nm, were obtained by Electrochemical Step Edge Decoration (ESED). The selective electrodeposition of metal at step edges. Nanowire growth by ESED was accomplished on highly oriented pyrolytic graphite surfaces by applying three voltage pulses in succession: An oxidizing activation pulse, a large amplitude, reducing nucleation pulse, and a small amplitude, reducing growth pulse. The activation pulse potential was optimized to oxidize step edges on the graphite surface just prior to deposition. The nucleation pulse had an overpotential for metal deposition of between -200 and -500 mV and a duration of 0.5-10 ms. The growth pulse had a small deposition overpotential of less than -100 mV. Nanowire growth was characterized by a time-independent deposition current and consequently, the nanowire radius was proportional to the square root of the deposition time in accordance with the expected growth law.

The metal nanowire arrays prepared using this approach may be lifted off the graphite surface, and incorporated into chemical sensors. Examples of such sensors will be described in this presentation.

SESSION H6: PHYSICS, CHEMISTRY AND MODELING OF NANOSTRUCTURES
Chair: Lhadi Merhari and Thomas Orlando
Wednesday Afternoon, December 4, 2002
Room 309 (Hynes)

1:00 PM H6.1
BIOLOGICALLY INSPIRED CONTROLS OVER ASSEMBLY OF CRYSTAL-NANOSTRUCTURES. J.J. De Yoreo, C.A. Orme, S.R. Qiu, C.L. Cheung, Lawrence Livermore National Laboratory; P.M. Dove, K.J. Davis, Virginia Polytechnic Institute; M. Kurimoto, B. Kahr, University of Washington, Seattle, WA.

By utilizing small molecules, peptides, and proteins to modulate crystal nucleation and growth, living organisms produce topologically complex 3D single crystals and crystal composites. They exhibit control over the location, phase and crystallographic orientation of the nuclei, as well as morphology and kinetics of the growing crystals. A common paradigm for interpreting this phenomenon asserts that the stereochemistry of the modifier is matched to that of a particular crystallographic plane that would otherwise be expressed during nucleation or growth. Here we review the results of AFM-based investigations into the control of surface and solution chemistry on nucleation and growth in many crystal-impurity systems. We have utilized the AFM as a "dip-pen" to create chemical templates for nucleation and performed in situ imaging of growth during the introduction of both inorganic and organic impurities into the solution. The systems examined include carbonates, phosphates, oxalates, and phthalates nucleated on alkanthiol SAMs or grown in the presence of amino acids, and organic dyes. In all cases, the growth kinetics and resulting crystal habit are defined by modifications to existing atomic steps and these modifications vary dramatically depending on the step direction, even on a single crystal face. While the exact mechanism of growth modification is different in each system, one common feature is that the important molecular-scale interaction that gives rise to growth modulation is between the impurity and a specific set of steps. These results show that, while control over nucleation may be understood within the paradigm of sterochemical recognition, to understand the controls on growth kinetics and morphology, a model that emphasizes the importance of step-specific impurity interactions on existing faces is more appropriate. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

2:00 PM H6.2

The manipulation of physical interactions between structural moieties on the molecular scale is a fundamental hurdle in the realization and operation of self-assembled materials and high surface area microsystem architectures relying on phenomena such as self-assembly, fluid flow, and interfacial tribology. The introduction of reversible photo-tuned interactions by photoactive molecules provides optical activation of nano-interactions impacting behavior on the nano- and microscales. We present observations on the surface characteristics of organic structures with known photophysical 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 NANOPARTICLES TO CARBON NANOTUBES BY CHEMICAL MANIPULATION. Kuiyang Jiang, Amir Eitan, Linda S. Schaefer, Palcik M. Aykan, 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 nanotubes have been incorporated into templates to fabricate some intriguing nanostructures. In this study, we present the anchoring of gold nanoparticles to carbon nanotubes by chemical modification of the carbon nanotube walls using a template to fabricate some intriguing nanostructures. The approach used is simple and versatile, and can be used to attach many other nanoparticle types (e.g., semiconductor nanocrystals, magnetic nanoparticles, etc.) to the carbon nanotubes.

2:20 PM H6.4

Monolayer-protected nanocrystals possess unique optoelectronic properties that can be tuned by adjusting the cluster composition, dimensions and capping layer chemistry. Interfacing these nanocrystals using molecular connectors allows us to fabricate 2D assemblies of interest for harnessing these properties in creating larger scale devices. Here, we describe phase transitions in 3D assemblies of octanethiol (OT)-capped nanocrystals of Ag and Au and CdS of sizes ranging from 2 to 10 nm. We use a combination of differential scanning calorimetry (DSC), transmission electron microscopy (TEM), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and in situ polarized microscopy (PLM) in our studies. DSC measurements reveal two melting-type reversible transitions at ~67 and 125°C in assemblies of OT-capped Ag nanoclusters, which are solids at room temperature. TEM of the assemblies showed interlinked nanoclusters in a close-packed configuration, due to hydrophobic interactions between the OT caps. Neither the nanoclusters nor their assemblies show observable structural changes after thermal cycling, indicating that the phase transition is of interest for harnessing these properties in creating larger scale devices. These results show that the phase transitions are due to OT, PLM and IR measurements show the first transition corresponds to the melting of a phase comprised of excess OT i.e., those not attached to the nanoclusters. The second transition corresponds to the "melting" of the nanocluster assembly due to increased mobility of the OT molecules that cap the cluster with alkyl chains attached to adjacent nanoclusters. Heating above 150°C leads to the disappearance of the phase transition during subsequent cooling and heating, indicating desorption and breakage of OT caps. Unlike Ag-OT, Au-OT and CdS assemblies are liquids at room temperature. Au-OT shows only one reversible 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 nanoclusters.

2:45 PM H6.5
CRITICAL UNIVERSALITY 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 study of the microstructural properties (grain size, grain size distributions and grain boundaries are modeled using a new algorithm. Using the cluster algorithm, we calculated
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 Ising model remain the same as those in the pure system. The nanocrystalline Ising system, therefore, remains in the same universality class.

3:30 PM H6.6 SUPERCONFORMAL FILM GROWTH IN SUBMICRON FEATURES. T.P. Moffet, 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 model has 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. Oles Kukenson, Anna Bahaz, Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA; David Jasnow, Physics Department, University of Pittsburgh, Pittsburgh, PA; Julis Yoonmas, 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 effectively semi-infinite layered solids or infinite planar films, resulting in one- or two-dimensional heat flow. However, only certain simple 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 nano-scale 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 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 material 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 nano fabrication process. This is especially true in three-dimensional fabrication and for features sized accordingly 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 kitchen flatware and 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 process. 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 mm-wave communications. These structures cannot be easily 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. The system of carbon particles was processed in electrical field in polymer melt with controlled ionic 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 are interpreted in terms of DLVO 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 phases of the assembly of carbon colloids: lateral vacuum + axial vapor (VAPOR), lateral liquid + axial vapor (COLLUMNAR LIQUID CRYSTAL), lateral liquid + axial liquid (SMECTIC LC), lateral liquid + axial solid (NEMATIC LC), and lateral solid + axial solid (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 permittivity for super-capacitors can be induced in appropriate electrical field in a polymer melt with effective ionic concentration. References [1] Bouda, V., Chladke, J., Carbon, 2001, 2, 127-133.

SESSION H7: POSTER SESSION SYNTHESIS, PROPERTIES AND APPLICATIONS OF 1D/2D/3D NANOSTRUCTURES Chairs: Lhadi 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). Leif Xu, Vincas 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 nanofabrication technology opens up new avenues to manipulate magnetic materials, and create novel architectures for engineering new materials, devices, and for obtaining better insight into micromagnetism. We have utilized the dip-pen nanolithography (DPN) approach to pattern soft and hard magnetic nanostructures. This is accomplished in two different ways. The first way, 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 magnetic oxide suspension of magnetic oxides (Fe2O4, MnFe2O4) to allow colloidal nanoparticle 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 surfaces. The precursor pattern is then directly converted to hard

Current optical based lithography is now reaching its limits of resolution, while electron beam lithography, that offer low cost, high throughput processing 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 the dissolved nanorods can be further functionalized or serve as templates for hollow polymer nanococoons.

H7.4 FORMATION OF CARBON NANOTUBES ON NICKEL FILMS/PARTICLES USING CVD. Stefanie Bassana and Al Sacco Jr., Center for Advanced Microscopy 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/silica). 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 5-10 nm. Thin nickel films were produced by evaporation at 10^-7 Tov. These nickel films were exposed to flowing hydrogen (20 ML/s, STP) at 1173 K. Their initial thickness controlled the height and diameter of the semi-hemispherical particles on a continuous nickel film resulting from hydrogen embrittlement. 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 45 nm to 10 nm ± 10%. These nickel particles were exposed to a mixture of 5 gases including H2, CO, CH4, CO2 and H2O at 20 ML/s (STP) at 1000 K and 1 atm. The gas phase carbon activity (aC) was controlled at 10, while the stoichiometry O/H in the gas phase was set at 0.1. TEM 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 20nm ± 1.5nm, at which point the density of nucleation diminished. Increasing (aC) to 20, while the other parameters remained constant, increased the nucleation rate of CNT formation 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 CHARACTERISATION OF CATALYST-FREE CARBON NANOTUBES FROM SILICON CARBIDE PRECURSORS. Eleon S. Humphreys, Bethany Andrews, John B. Vander Sande and Yet-Ming Chiang, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Catalyst-free nanotubes have been produced by the high temperature active oxidation of SiC. Selective growth of carbon nano-tubes (CNT) on micron scale using scanning electron microscopy (SEM) and Raman spectroscopy. These novel high-purity nanotubes, and their use in phase display experiments, are the topics of two other papers at this meeting. This research is supported by ONR Grant No. N00014-98-1-0354 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 Chopra, Bruce Hinds, 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 micron scale 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 (Dai Qian Ph.D. dissertation 2001 University of Kentucky, Wei et al 2003 Nature 42, 495 2003 University of Kentucky, Wei et al 2003). Using a commercial oil press the pattern of the imprint mold is directly transferred into a mixture at 700C. CNTs are observed to grow only on the exposed SiO2 surface at the edge of the "mesa" structure. This allows the precisely controllable thickness of a SiO2 film to determine an exposed SiO2 line width. There is no need for e-beam lithography since film thickness determines nm-scale dimensions. CNTs are then formed by CVD with a ferrocene/H2Ar mixture at 700C. CNTs are formed to grow only on the exposed SiO2 surface at the edge of the "mesa" structure. CNT diameters of 13.2, 20.5, 34.2, 64.3nm are observed for SiO2 film thickness of 12, 19, 38, and 65 nm. Standard deviation are 1.4, 3.8, 6.7 nm 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. CNT's growing from this "mesa" edge process have applications for interconnections, NEMS or can be removed for later self-assembly into chemically defined structures.
carbon nanotubes (CNTs) are potential candidates for a variety of new types of devices and some interconnect applications. High mechanical strength combined with good heat conductance and a range of attractive electrical properties make CNTs particularly interesting building blocks for rapidly emerging nanoelectronics and nanoeengineering. For nanoscale devices based on carbon nanotubes, the performance will be crucially dependent upon the quality of the interfaces, since the entire device may now lie within nanometers of the interface. Successful integration and nanoeengineering of the nanotubes with metal requires understanding of the effects of the metal fabrication process on the structure and chemistry of the nanotube, and on 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 nanoeengineering purposes. The quality of the interface between CNT and the metal contact line 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 both 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 FIB-assisted Pt deposition on multi-wall nanotubes were studied 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 layers as a function of FIB imaging and deposition parameters are presented. FIB parameters are optimized to provide the non-destructive imaging and controllable Pt deposition with minimal damage on 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. Beerbom, University of South Florida; D.A. Walter, University of Central Florida; Z.P. Ren, Z.P. Huang, Boston College; B.B. Rossie, Agere Systems; and A. Schmal, University of South Florida.

Well-defined carbon nanotubes (CNT) were grown on the apexes of standard Si atomic force microscopy cantilevers. CNT probes are thought to be ideal atomic force microscopy (AFM) probes for use in high aspect ratio critical dimension metrology (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 standard Si atomic force microscopy cantilevers. CNT probes are thought to be ideal atomic force microscopy (AFM) probes for use in high aspect ratio critical dimension metrology (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. 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H7.9 BUILDING MACRO-SCALE NETWORKS AND BRIDGES OF ALIGNED CARBON NANOTUBES. Anyuan Cao, Binging 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 mesoscale 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 quartz tube, where they deposit onto arrays of relief metal structures 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 strength cips in aero-space and telephone-pole type configurations are aligned along the gas flow direction. 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 surfaces 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 anodization lithography for achieving the vertical alignment of SWNTs with surfaces. 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 oriented SWNTs, and the distribution of the vertically aligned SWNTs is consistent even after the prolonged reaction time. The aspect ratio of SWNTs aligned on Si 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 sides of nanotubes described as "nucleation growth". Longer tubes get adsorbed on the surface by increase in the bundle size and nanotube length, simultaneously. Based on the chemical reactions of the modified SWNTs with functionalized surfaces, selective attachments of SWNTs were carried out onto pre-patterned surfaces. Detailed characterization of aligned SWNTs will be discussed.

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

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-aminopropyl triethoxysilane (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 blocks is of interest for hybrid and nanodevices. Carbon nanotubes (CNTs) linked with nanoclusters is a striking example of such a unit that will allow the exploration and tuning of unique electrical and/or optical properties of nanotubes and 3D quantum dots. Here we demonstrate for the first time the attachment of Au nanoclusters to CNTs via hydrophobic interactions between self-assembled molecular monolayers of octanethiol molecules covering the nanotubes, and acetone molecules activating nanotube surfaces. HRTEM and OS measurements show that interlinked assemblies of Au nanoclusters with average size of ~3 nm are attached to the multilayerd CNTs 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 FTIR spectroscopy, 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; Bingying 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 fullerenes and carbon nanotubes, in particular their two-dimensionality and high surface area. Under typical growth conditions, the as-grown nanowalls 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, catalysts, and light emission / detection, field emission and biomedical devices. The results on the growth of Ni, NiCoFe, Fe, ZnO, TiO_, InO_, SiO_, 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. Wu YH and Yang BJ, Nano Letters 2 (4): 355-359 APR 2002.

H7.16 EFFECT OF SITE DENSITY OF ALIGNED CARBON NANOTUBES ON ELECTRIC FIELD SCREENING. Yi Tu, Zhongqiang Huang, Dezhi 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 10^4 to 10^6/cm² and length of 1, 5, 10 μm have been studied in this work.

H7.17 Abstract Withdrawn.

H7.18 FABRICATION OF CARBON NANOTUBE LATERAL FIELD EMITTERS. A.S. Teh, K.B.K. Teo, Manish Chhowalla, W.J. Milne, G.A.J. Amarasingha, Cambridge University, Engineering Dept., Cambridge, UK; Padmakar Kichambare, University of Kentucky, Dali Qian, David Jacques, Rodney Andrews, University of Kentucky, Data Storage Institute, Singapore, Dept of Physics, Singapore and Data Storage Institute, SINGAPORE.

We recently reported on the growth of single crystal ZnO nanorods using catalyst-driven molecular beam epitaxy. ZnO nanorod nucleation was achieved via nucleation on Ag nanoparticles that are distributed on a SiO2-terminated Si substrate surface. In this talk, 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 a recent work, the bandgap of ZnO (Eg = 3.37eV) can be modified via alloying with MgO. Photoluminescence of Zn1-xMgxO nanorods shows a peak shift to higher energy with increasing Mg into the transport properties of the Zn1-xMgxO nanorods. The synthesis and properties of these structures will be reported, including photoluminescence, microstructure, and TEM data. The site-selective, in situ formation of Zn1-xMgxO nanorods and nanowires may prove attractive for nanodevice concepts.
ZnO NANO/WIRE GROWTH ON VARIOUS SUBSTRATES BY CVD THROUGH VAPOR-LIQUID-SOLID CRYSTAL GROWTH MECHANISM. Hyun-Gi Hong, Jung Inn 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, sapphire, 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 10\(^{-6}\) Torr. We found that the metal thin film was broken to nanoparticles during the CVD growth. Metal thin films are deposited on various substrates by a pulsed laser deposition technique under a pressure of 10\(^{-6}\) 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. Nanowires were deposited on a substrate 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 20 to 100nm in diameter and a few micrometers in length. From the analysis of Rutherford backscattering spectroscopy, we found that the orientation of ZnO nanowire is a wurtzite structure. PL spectra of ZnO nanowire were measured with a He-Cd laser (325nm) of excitation power of 20mW. The full width at half maximum (FWHM) of 52.09 meV was observed.

CONDUCTING NANO/WIRES AND NANO/TUBE MATERIALS PREPARED FROM POLYMER FIBER TEMPLATES. Hong Dong, Yongwon Cho, Kyu-Young Koo, and Seung-Woo Lee, 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. The effort to prepare novel and electrically conducting nanomaterials, we have recently prepared extremely low dimensional conducting nanowires and fibers from conducting polymers (e.g. polyaniline, polypyrrole) using an electrostatic, non-mechanical “electrospinning” method. Insulating Polypyrrolactide (PLA) fibers with average diameter of 200-700nm were initially fabricated as core materials. 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 of 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 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.

UNIDIRECTIONALLY ORIENTED NARROWBAND-DYE HYBRID MATERIALS CREATED BY SELF-ASSEMBLY AND ELECTROPHORESIS. Leiming Li, Guizhong Zhang, John C. Stendahl, Eugene R. Zubarev, and Samuel I. Stupp, Department of Chemistry, Medical School, Northwestern University, Evanston, Ill. Dendron rodcoil (DRC) molecules contain covalently connected dendron-like, and corona segments, and form gels with certain solvents like styrene or 2-ethylhexyl methacrylate (EHMA). Gelation is triggered by the self-assembly of DRC molecules into a network of ribbon-like 10nm wide, 2nm thick, and up to 10 microns long. When subject to a DC electric field, electrophoresis occurs in the DRC-EHMA gel, creating thin solid films consisting mostly of DRC nanoribbons oriented preferentially along the polymerization direction. Small weight percentage of certain dye molecules, such as disperse red 1 (DR1), was dissolved in the gel. Similar electrophoresis creates hybrid films of unidirectionally oriented DRC nanoribbons and DR1 molecules. Strong emission polarization was obtained from the embedded DR1 dyes, significantly larger than that obtained from DR1-polystyrene samples stretched up to 22 times their original length. Interestingly, no obvious decrease in emission polarization was observed after the oriented nanoribbon-DR1 films were annealed at 100°C.


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 geometry 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 straight forward 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.

Abstract Withdrawn.

RATIONAL CONTROL OF NANOSCALE HELICAL MORPHOLOGIES THROUGH BINARY SELF-ASSEMBLY. George John, Joon Hwa Jung, Kaname Yoshida, Hiroyuki Minamikawa, Toshimi Shimizu, CREST, Japan Science and Technology Corporation, Nanoscale Technologies 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 fibrous 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 morphologies has been achieved by binary self-assembly of the saturated and monoenic derivatives. This method can provide the generation of a diversity of self-assembled high-surface ratio nanostructures (HSRN) ranging from, twisted ribbons, helical ribbons and nanotubes.

SYNTHESIS BY SELF-ASSEMBLY OF IRON-COBALT NANO¬ALLOYS. Melissa Zubris, Rina Tannenbaum, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

Nanoparticles, i.e. alloys formed via the co-aggregation of different metals at the nanoscale, represent an exciting new area in nanotechnology. These nanotubes have unique properties that neither the bulk alloys nor the discrete atoms possess. Gold and silver nanoclusters have been used to produce nanotubes, but no such systems have yet been reported with transition metals. In this paper, we are presenting the synthesis of iron and cobalt nanotubes 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 nanoclusters with cobalt nanoclusters will form new nanotube compositions with good magnetic properties and interesting potential applications. In order to form iron-cobalt nanotubes 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 studied. 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 nanotubes using carbonyl precursors.

ORGANIC MOLECULES ACTING AS TEMPLATES ON Cu(110). Federico Roset, V. Naitoh, M. Schanack, E. Leggaard, I. Stengaard, and F. Besenbacher, Physics Department and L-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim CEMES - CNRS Toulouse, FRANCE.
Large organic molecules have recently attracted interest from a fundamental point of view and for prospective applications in nanotechnology, because they are the basic building blocks for molecular electronics devices [1]. We investigated the adsorption of Lander molecule [2] (C90H198) on Cu(110) by Scanning Tunneling Microscopy (STM) at 300-350 K. The Lander has a central polycrystalline molecular wire (conducting backbone), and four "spacer legs" (3,5-di-tert-buthylphenyl) for isolation from the substrate. The four legs are imaged with different conformations by STM. Manipulation experiments with the STM at low temperatures on isolated Lander molecules adsorbed on step edges reveal a restructuring of the step edges [3]. On removal from a step, a tooth-like nanostructure appears. The structure's width is two atomic rows, corresponding to the distance between the spacer legs within the molecule. This process is thermally activated; repeating the same manipulation experiments on molecules adsorbed at low temperatures (150 K), no restructuring of the step edges is found. In a second set of experiments, the clean Cu(110) surface was exposed to oxygen to form oxygen-induced (2x1) reconstruction surface. By dosing a proper amount of O2 at 350 C we nanopatterned the substrate into Cu trenches along the [011] direction with 3 nm width, with a periodicity of about 5 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 1 D 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 397, 674 (1999). [2] C. Joachim et. al., Molecules acting 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. Guangwen Zhou, 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 oxidation process. In-situ observations can provide insights into distinguishing between morphologies due to kinetic or thermodynamic considerations. It is reasonable to expect that temperature would affect the kinetics and/or energetics of the oxide formation. We have systematically investigated the dramatic effect of temperature on the oxide formation due to in situ oxidation of Cu(001) and modeled some of the morphology changes. We demonstrated that dramatically different morphologies of oxide nanostructures can be achieved by modifying the oxidation temperature. Kinetic and thermodynamic factors 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 oxidation process. The innate pore-solid architecture of aerogels, which are low density, amorphous and non-conducting networks of silicate (or titania) sol serves as a nanoglue to produce a diverse range of nanostructured hydrogels. Novel hydrogels with mesoscopical crystal structures have been synthesized and characterized. First, monodisperse N-isopropyl-acrylamide (NIPA) co- 2-hydroxyethyl acrylate (HEAc) hydrogel nanoparticles were made using emulsion polymerization. And then hydrogel crystals were created by covalently bonding the self-assembled nanoparticles using crosslinker divinyilsulfone (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 properties and are excellent for application in microelectronics, optics, magnetics and microelectromechanical systems. We have developed a fluid-forming process for self-assembly of particles into planar arrays 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 will focus on the preparation of <001>-oriented Pb(57.5Tl)O3 arrays using cube-shaped particles. Field emission scanning electron microscope (FESSEM) and imaging analysis results showed 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 along the x-y plane. These dense-packed <001>-oriented PZT planar arrays can be further processed as textured composites or textured single-phase materials.


Recently, nano-sized spherical titania has been of interest as colloidal crystals for photonic band gaps due to their large refractive index in the optical regime (n~2.5). In order to obtain these novel crystalline materials the particles need to be grown with as little as 5% error. They are typically assembled into photonic band gap structures (e.g., FCC) by self-assembly processes by one of the following methods: confined assembly, sedimentation growth or electrostatic interactions. Therefore, there is a need of controlling the size and shape of these oxide materials. In this paper we report the development of new morphology control of titania by wet chemical methods so as to produce spherical sub-micron and micron size titania. The method of preparing these materials and characterizing by SEM and light scattering methods will be discussed.


The innate pore-solid architecture of aerogels, which are low density, amorphous and non-conducting networks of silicate (or in some instances, titania) sol serves as a nanoglue to produce a diverse range of composite aerogels incorporating particulate guests. Particles ranging in size over six orders of magnitude (from a nanometer, which is smaller than the domain size of the silica, to a millimeter) can be accommodated in the aerogel host. The chemical nature of viable guests ranges from metal to metal oxide, carbon, ceramics 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. Xihua Lu, Zhuibing 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 (NIPA) co- 2-hydroxyethyl acrylate (HEAc) hydrogel nanoparticles were made using emulsion polymerization. And then hydrogel crystals were created by covalently bonding the self-assembled nanoparticles using crosslinker divinyilsulfone (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 properties.
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 POLYMORIZABLE COMPLEX METHOD. E.R. Leite, N.L.V. Carreño, E. Longo, J.F.R. Baptista and F.M. Pontes. IME-UNICAMP, Departamento de Química, UFSCar, Sao Carlos, SP, BRAZIL; A. Barison, A.G. Ferreira, Departamento de Química, UFSCar, Sao Carlos, SP, BRAZIL; J.A. Varela, Instituto de Química, UNESP, Araraquara, SP, BRAZIL.

This work presents the synthesis and characterization of SiO₂-metal (Ni, Co, Ag and Fe) nanocomposites processed by the Polymizable 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 macromolecule chain and the transition metal cation embedded in a amorphous matrix formed by SiO₂ and carbon. In the SiO₂-Fe system, Fe₃C was also detected by XRD.

H7.35 SELF-ASSEMBLED ORGANIC/INORGANIC NANOCOMPOSITES. Byron Mccaughey, Donghai Wang, Eric Hampsey, Xianglin Ji, and Yunfeng Lu. Chemical Engineering Department, Tulane University, New Orleans, LA.

Nanostructures 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 areneethynelene polymers, ethylene polymers, or dicetylene 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 NANOPARTICLE INKS FOR DIRECTED ASSEMBLY OF 3-D PERIODIC STRUCTURES. Qi Li, Gregory Graso, and Jennifer A. Lewis. University of Illinois, Urbana, IL; James Smay, Oklahoma State University, Stillwater, OK.

Nanoassembly 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 development of mesoscale nanostructures 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 robotically 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. Hirokazu Tada, Masato Ara, Shoji Tanaka, Institute for Molecular Science, Okazaki, JAPAN.

Alkyl monolayers anchored covalently on silicon were prepared through the reaction between alkylsilanes and hydrogen-terminated silicon (111). The 2D-patterning of the surface was done by local oxidation with an atomic force microscope (AFM) and 3-D molecular assemblies were fabricated by molecular planting in a specific site of the surface. The surfaces were aerotherm with a contact-mode AFM by applying the negative bias voltage to the surface with respect to a platinum-coated cantilever under ambient conditions, which resulted in nanometer-scale oxidation of surfaces. The threshold voltage was 5V for anodization of silicon covered with a dodecyl monolayer, which was lower than that for silicon examined in vacuum. 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 planned arynamine molecules to which organic dyes such as fluorescein and porphyrin were anchored through amide-couplings. The interaction of luminescence 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 NANOPARTICLES. Benjamin L. Frankamp, Andrew K. 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 nanocomposite materials. We have used poly(amideamine) (PAMAM) dendrimers to assemble carboxylic acid-functionalized mixed monolayer protected clusters (MMPCs) through acid/base chemistry between particle and polymer. IR spectroscopy and selective dendrimer stainer, observed by Transmission Electron Microscopy (TEM), can establish 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. The X-ray diffraction patterns for 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 (Tₜ) 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 NANOPARTICLES: BUILDING BLOCKS FOR NANOTECHNOLOGY. Franz Redl, Stephen O'Brien, Ming Yin, Stephanie Granzhov, 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 structures that will have function and utility. Physical, chemical, optical, magnetic or electronic properties of nanostructured materials can be tuned by adjusting size, shape and surface-modification in order to take advantage of nanoscale materials we seek to control their arrangement into usable dimensions. A nanoscale approach to this issue combines the advantage of simplicity 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 surfactants). We describe the formation of 3-D and three-dimensional nanocrystal superlattices of magnetic iron oxide nanoparticles forming a framework of superparamagnetic spheres and semiconducting lead selenide nanoparticles. The crystals were obtained by self-assembly of materials during co-crystallization from solution. We are exploring routes to novel synthetic 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 bio-compatibility 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 monodispersed nanoparticles of γ-Fe₂O₃ and are pursuing similar techniques for the other iron oxides. Fe₃O₄ (magnetic) and γ-Fe₂O₃ are both ferrimagnetic making them interesting to models to explore magnetic stability and the self-assembly in ferrimagnetic systems.

H7.40 SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES OF Fe₃P₁₅₋ₓCu₁₅ NANOCOMPOSITE PARTICLES. Xiang-Cheng Sun,
Fe₃PₓCu₁₋ₓ nanoparticles were synthesized by simultaneous chemical reduction of platinum acetylacetonate and copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) and thermal decomposition of iron pentacarbonyl. The relative amounts of iron, platinum and copper in the particles depended on the amount of iron, platinum and copper charged to the reaction. As-made the particles possessed a disordered face-centered cubic (FCC) lattice with an average diameter of 3.5 nm and were superparamagnetic. These particles were well dispersed in hydrocarbon solvents and self-assembled into granular films when deposited onto carbon coated Cu TEM grids or single crystalline Si(100) substrates. After ex-situ annealing from 500°C to 700°C under an Ar+H₂ atmosphere, the particles transformed into the tetragonal phase (L₁₀, PCT). The coercivity (Hₘ) of the annealed film decreased due to surface magnetically soft phase on annealed sample surface. The above results were very different with sputtered Fe₃PₓCu thin films.

**Molecular-Dynamics Study of the Mechanical Properties of Metal Nanowires.** T. Nakajima, K. Shintani, Univ. of Electro-Comm., Dept of ME & Intelligent Sys, Tokyo, JAPAN.

Observations of single arrays of metallic atoms in scanning tunneling microscopy studies have provoked proposals of applications of nanowires. Nanowires have some unique properties at their nanoscale such as quantized conductance and long bond-length which are not observed for materials at the larger dimensions. It can also be expected to be a microscopic behaviors of nanowires under external forces, e.g. their stress-strain relationship and plasticity, are different from the ones of the macroscopic materials. In this study, molecular-dynamics simulation is employed to study deformation of metal nanowires on a tensile process begins, a model nanowire is equilibrated at a specified temperature. A few layers at one end of the nanowire are kept fixed. A few layers at the opposite end are forced to be displaced until the nanowire breaks. The deformation is observed throughout the tensile process. How the structural anisotropy of nanowires affects their deformation behaviors and mechanical properties is investigated.

**Effective Medium Calculations of the Electromagnetic Behavior of Single Walled Carbon Nanotube Composites.** John W. Schultz, Georgia Tech Research Institute, Atlanta, GA.

The high aspect ratio and unique conductive behavior of carbon nanotubes provide opportunities for new composite materials with useful RF and microwave properties. Coating or filling carbon nanotubes with insulating or metallic materials can provide further enhancements to their electromagnetic properties. Some applications in EMI and telecommunications require lightweight conductive materials while other applications call for low loss substrate materials with high dielectric constant. In this study, the electromagnetic properties of single walled carbon nanotube assemblies were calculated with an effective medium approximation at frequencies from 200 MHz to 200 GHz. The model treats the carbon nanotubes as layered cylinders, each with a core, a graphene layer and an outer layer, to investigate the dielectric properties of coated and filled nanotubes. The graphene and metal layer properties were modeled with a Drude approximation based on literature data. A generalised Bruggeman model was then used to determine the macroscopic behavior of the modified carbon nanotubes in a composite structure as a function of volume fraction, frequency, and aspect ratio. The depolarization factors in this model were scaled significantly. XRD patterns indicated that even the chemical ordering improved with annealing at higher temperatures (> 550°C), a ternary Fe₃PₓCu alloy phase was found on the exfoliated surface of the Co-Cu TEM grids or single crystalline Si(100) substrates.

**Session H8: Fabrication and Properties of Nano-sized Materials**

**H8.1 Three-dimensional Nanostructure Fabrication by Focused-Ion-Beam Chemical Vapor Deposition.** Shinji Matsui, Himeji Institute of Technology, Kamigori, Ako, Hyogo, JAPAN.

Two-dimensional nanostructure fabrication using electron-beam (EB) and focused-ion-beam (FIB) has been achieved and applied to make various nanostructure devices. Ten-nm structures are able to be formed by using a commercial available EB or FIB system with 5 nm beam diameter and high-resolution resist. In this way, it is considered that the technique of two-dimensional nanofabrication has been established. On the other hand, three-dimensional nanostructure fabrication has been also studied using both EB and FIB induced deposition (CVD). The deposition rate of FIB-CVD is much higher than that of EB-CVD due to factors such as the difference of mass between electron and ion. Furthermore, FIB-CVD has an advantage over EB-CVD in that it is more easily to make a more complicated 3-dimensional nanostructures. Because, a smaller penetration-depth of ion compared to electron allows to make a complicated 3-dimensional nanostructures. For example, when we make a coil nanostructure with 100 nm linewidth, electrons with 10-50 keV pass the ring of coil and reach on the substrate because of large electron-range (over a few 10 nm), so it is very difficult to make a coil nanostructure by EB-CVD. On the other hand, as ion range is less than a few 10 nm, ions stop inside the ring. This paper presents a complicated 3-dimensional nanostructure fabrication using FIB-CVD. A carbon-coil with 500 nm diameter and 80 nm linewidth, which was made by 30 kV Ga⁺ FIB with carbon containing source (phenanthrene) gas. This demonstrated that FIB-CVD is very useful to make a complicated 3-dimensional structures. Moreover, we report an evaluation of the Young modulus of such amorphous carbon pillars by measuring the resonant frequency of pillars. The spontaneous vibration of pillars was detected in SEM electron beams, and the resonant characteristics were analyzed through the signals of a secondary electron detector.
Kazuki Takashima and Yakichi 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 growth, etc. Using these methods, however, it is difficult to obtain the grain size of NCs less than 10 nm. One of the attractive ways to control the structure of materials in the order of several nanometers is ion beam irradiation. Up to now, most ion beam irradiation studies have been performed on crystalline materials, with little on amorphous alloys. Amorphous alloys are in a thermally nonequilibrium state, so that crystallisation may occur under ion beam irradiation, but details have not been clarified. In this study, we have examined the structural change of an amorphous alloy under ion beam irradiation. The material used in this study was a Ni-11.5wt%P amorphous alloy. Specimens were fabricated into a circular disk with a diameter of 3 mm. Prior to ion beam irradiation, two kinds of implantation beams, the power of one and one fifth, were used with ion sources of Ga and Ar respectively. Transmission electron microscopy observation of the area revealed the formation of NCs with grain sizes of approximately 5 nm in the amorphous matrix with both ion sources. The crystalline structure of NCs was determined as a fcc from electron diffraction analysis. Furthermore, the NCs formed a crystallographically orientated relationship with the matrix, that is, a (111) of NCs was parallel to the irradiated surface. NCs had a specific orientation relationship with each other in the irradiated plane. The results suggest that ion beam irradiation techniques have the possibility to form three-dimensionally orientated NCs in amorphous alloys. The mechanism of formation of crystallographically orientated NCs under ion beam irradiation will be discussed.


Conventional, broad-area, ion implantation through 3-d masks is a combination of chemical etching to create a pattern 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 thickness of the array determines the etching depth. The second example uses self-assembled, nanometer-sized hole arrays are produced by electrochemical etching in alumina. The porous alumina 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.

09:30 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, Timo Meyer-Friedrichsen, Valerie Alain, Stephens M. Kuebler, Seth R. Marder, Joseph W. Perry, 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 have a large one-photon absorption with its excitation in the region of a polymer matrix with a soluble silver salt (AgBF4) 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-nucleated metal crystals have been dissolved in the matrix. Tailor-made ligand-coated metallic nanoparticles can be readily made and can be readily made and can be used in the study of 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-standing structures can be fabricated and characterized. Silver, copper, and gold microstructures will be presented. Finally, we will describe nanoparticle functionalized with covalently bonded dye: these particles can grow when the dyes are irradiated with light or electron-beams. P. W. Wu, et al., Adv. Mat. 12, 1438 (2000). 2. T. Deng, et al., An. Chem. 72, 645 (2000). 3. F. Stellauci, et al., Adv. Mat. 14, 194 (2002).

09:45 AM H8.5 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 unusual morphologies such as helices or chevrons. PTFs are fabricated using a template of nanosprings or nanochannels 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 nanostuctures. PTFs have been produced by filling template helical GLAD films with various substances, etching back the coating to reveal the tips of the helices, and etch removal of the helical template. We will report a range of novel nanosprings fabricated using the PTF technique, including ordered periodic arrays of helical perforations, utilizing a template of arrayed nanosprings. We are developing a protocol for fabricating metal PTFs in which electroplating is used to fill the original template. We will also report a replica process, using PTFs as a template, from which nanohelices can be fashioned in materials that cannot otherwise be used in the GLAD process, such as polymers. Results of characterization of these structures will be presented, including structural and optical analysis. Preliminary results show that helical PTFs have a structural optical activity.

10:00 AM H8.6 NANOTECTONICS: FABRICATION OF INORGANIC TRANSISTORS AND MICRO-ELECTRO-MECHANICAL SYSTEMS FROM NANOPARTICLE BUILDING BLOCKS. Joseph Jacobson, Eric Wilhelm, Colin Bulthaup and Brent Ridley, The MIT Media Lab Center for Bits and Atoms, Massachusetts Institute of Technology Cambridge, MA.

Recently the authors have developed an approach termed Nanotectonics for the all-printed fabrication of both inorganic logic elements (Science 286 (5440) 740) and micro-electro-mechanical systems (MEMS) using nanoparticle building blocks. Using this approach the authors have fabricated both inorganic transistors, including passive components such as resistors, capacitors, inductors and vias necessary for universal logic, as well as MEMS devices. We report on recent results using this approach.

11:00 AM H8.7 ASSEMBLY OF SEMICONDUCTOR AND MAGNETIC NANOCRYSTALS INTO BINARY NANOCRYSTAL SUPERLATTICES. F.X. Redl, IBM Corp; K.S. Cho, IBM Corp and University of New Orleans; C.B. Murray, IBM Corp, Yorktown Heights, NY.

We present the co-assembly monodisperse Fe203 nanocrystals and PbSe nanocrystals into a 3-dimensional nanocrystal superlattices with and AB13 intermetallic structure. Methods for direct the assembly of the nanocrystals will be discussed. The systematic to systematic structural characterization of these binary superlattices (colloidal crystals) will also be presented. These binary nanocrystal superlattices are a new class of magneto-optic composites.

11:15 AM H8.8 SYNTHESSES OF COMPLEX-SHAPED, 3D, SELF-ASSEMBLED NANOPARTICLE STRUCTURES WITH TAILORED CHEMISTRIES BY THE BASIC PROCESS. Frank Zalar, Matthew Dickerson, Raymond Unocic, Ken Sandhage, Dept of Materials Science and Engineering, Ohio State Univ, Columbus, OH; Rajesh Naik, Gunjan Agarwal, Morley Stone, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

A novel approach for fabricating large numbers of complex-shaped, three-dimensional (3-D) nanoparticle structures with tailored chemistries is presented: the Bielastic and Shape-preserving Inorganic Conversion (BiSIC) process. A "bielastic" structure is a mineralized object with a shape that has been retained through the action of a living organism. Among the most striking bielastic structures are the frustules of diatoms. Diatoms are single-celled algae...
that are ubiquitous to aquatic (marine and freshwater) environments. Diatoms form intricate 3-D frustules (microshells) comprised of assemblies of silica with calcite. The ratio of extant diatom species is \(10^6 \) to \(10^8\). Each species of diatom forms a frustule with a unique shape and with fine, distinctive features (e.g., pores, ridges, protuberances). Continued reproduction through active growth can yield large numbers (e.g., billions) of daughter diatoms with similarly-shaped frustules. Such massively parallel 3-D self-assembly of complex-shaped nanoparticle structures can be highly attractive for nanotechnological applications. However, the range of potential applications is limited by the silica-based chemistry of diatom frustules. The compositional limitations of bioclastic structures can be similarly-shaped frustules. Such massively parallel 3-D self-assembly 4. Each species of diatom forms a frustule with a

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actuated by the application of light. Spatially varying mechanical driving of micromechanical structures was also demonstrated using a scanning probe tip for actuation and an electron beam to detect motion. Sensor applications include immunospecific detection of single bacterial cells and chemical monolayers. Parametric amplification of mechanical signal that was demonstrated in a variety of device configurations, with optical and electrodynamic drive. High-resolution lithographic processes have been used to create similar resonant mechanical actuators with dimensions below tens of nanometers. The smaller devices are also more susceptible to surface related mechanical loss mechanisms, which we have begun to study. Related nanofabrication techniques have also been used to create nanostructures for the mechanical manipulation and sorting of molecules by mechanical and physical properties in a variety of fluid containing system configurations. Mechanical confinement of systems has also been used to enable optical detection and analysis of individual biomolecules.

2:45 PM *H0.4* OPTICALLY DRIVEN MICROMANIPULATION TOOLS MANUFACTURED BY TWO-PHOTO ABSORPTION LITHOGRAPHY. Shoji Maruo, Koji Ijutsu and Hayato 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 nanoscale science and technology. A variety of manipulators such as carbon nanotube tweezers and micromachined nanotweezers have been developed for grabbing or probing micro/nano scale objects. However, these tweezers are based on electrostatic forces, and are not ideal for aqueous solution work such as manipulation of cells, microbes and single molecules. In this paper, we report optically driven micromanipulators suitable for biological applications that require work in aqueous solution. Our manipulators were fabricated by using two-photon photomicrostereolithography [1, 2]. These micromanipulators are driven by optical trapping based on radiation pressure from a tightly focused laser beam. Since optical trapping enables remote drive of movable micromechanisms in biological fluid environments, the micromanipulators are well suited for the application in bionanotechnology. 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 are 8.7 μm long and 1.7 μm 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 10–19 Nm. Finally, we developed microtweezers and microneedle 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.


3:00 PM *H0.5* BIOLOGY DOES IT DIFFERENTLY. HOW CAN WE HARNESS ITS ADVANTAGES? Daniel E. Morse, Jan Sumerel, Wenhui Yang, James T. Neade, Timothy Deming, Bradley F. Chmelka, Galen D. Stucky and Paul K. Hansma, University of California at Santa Barbara, Biomolecular 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 stenciled vapor deposition strategies are used in current manufacturing technologies to produce multi-layered structures for microelectronics, the biological mechanism underlying formation of the microcrystalline rubber-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 the bilaminate composite, mostly organized in a two-dimensional lattice, strongly contributing to the toughness of these materials. While this mechanism generates the hierarchically organized bone-like nanostructures of silica produced biologically in sponges 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 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 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 the surrounding lipid membranes. Higher-order branching of silica capsules in sponges 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 *H0.6* 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 methods have been applied to fabricate micro/nano structures for the purposes of drug delivery, gene transfer, and tissue engineering. A number of methods have been developed, including photolithography, etching, and deposition. These methods are currently being applied to fabricate 3-dimensional structures that can be used in biomedical applications.

4:30 PM *H0.7* BIO-INSPIRED SELF ASSEMBLY OF MICRO- AND NANO-STRUCTURES FOR SENSING AND ELECTRONIC APPLICATIONS. H. McNally, S.W. Lee, G. Guo, M. Pingle, D. Bergstrom, R. Bashir, Dept. of Electrical and Computer Engineering, University of North Carolina, Charlotte, NC; S. W. Lee, D. Guo, M. Pingle, D. Bergstrom, R. Bashir*,  "School of Electrical and Computer Engineering, Department of Mechanical Engineering, 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 sensing 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 bio-nano-composite packaging. Fluorescein conjugated streptavidin and Anti-Listeria Antibodies were patterned as a demonstration. To show its application in biological inspired self-assembly, this technique was successfully employed 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 receptors 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.

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