

SYMPOSIUM Y

Nanopatterning: From Ultralarge-Scale Integration to Biotechnology

November 25 – 29, 2001

Chairs

Kenneth E. Gonsalves

Dept of Chemistry
Univ of North Carolina
Charlotte, NC 28223
704-687-3501

Lhadi Merhari

CERAMEC R&D France
Limoges, F-8700 FRANCE
33-555-794005

Elizabeth A. Dobisz

IBM Almaden Research Ctr
K66/C2
San Jose, CA 95120
408-927-2923

Marie Angelopoulos

Adv Lithography Matls & Processes
IBM T.J. Watson Research Ctr
MS 19-203
Yorktown Heights, NY 10598
914-945-2535

Daniel J. C. Herr

Matls & Process Sciences
SRC
Research Triangle Pk, NC 27709-2053
919-941-9431

Symposium Support

CERAMEC R&D France
Motorola France
Nanoresist Technologies, Inc.
The Whitaker Foundation

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as Volume 705
of the Materials Research Society
Symposium Proceedings Series

* Invited paper

TUTORIAL

FT Y: NANOFABRICATION FOR CELLULAR ENGINEERING Sunday, November 25, 2001 2:00 p.m. - 5:00 p.m. Room 204 (Hynes)

This tutorial will address key issues of nanofabrication for biocompatible substrates. A review of the nanofabrication techniques suitable for patterning biocompatible materials will be given. The emphasis will be put on the effect of controlled surface topography on cell adhesion, growth and motility. Applications including in vitro engineered tissues and bone cells optimally grown on biodegradable templates will be described. A brief introduction to emerging biochips will then be given.

Instructors:

Mathis Riehle, Centre for Cell Engineering, Univ of Glasgow (UK)
Mehmet Toner, Harvard Medical School, Massachusetts General Hospital

SESSION Y1: ADVANCED MATERIALS AND PROCESSES FOR NANOLITHOGRAPHY I

Chairs: Kenneth E. Gonsalves and Lhadi Merhari
Monday Morning, November 26, 2001
Back Bay D (Sheraton)

8:30 AM *Y1.1

RESIST REQUIREMENTS FOR ELECTRON PROJECTION AND DIRECT WRITE NANOLITHOGRAPHY. L.E. Ocola, A.E. Novembre, Agere Systems, Murray Hill, NJ.

Aspects of resist properties required for nanolithography using high-energy electrons are described in this paper. High-energy electron lithography, such as Electron Projection Lithography (EPL) or Direct Write e-beam lithography (DW), does not have the absorption limitations encountered in DUV lithography and other optical lithography alternatives. With no opacity limitations, concentration levels and types of photo-acid generators (PAGs) can be added with more flexibility to make these resists more responsive to high-energy electrons, as long as development interactions and imaging quality are not compromised. This paper describes a series of experiments where by extrapolating from DUV and EUV resist concepts optimized e-beam sensitive resists can be obtained. This study shows that, as for DUV resists, intercomponent interactions between PAG, base and polymer resin are crucial for image formation. Optimization of the resist processes requires a detailed understanding of the image formation process during exposure. This process has been simulated using discrete models from exposure through development for a positive EPL or DW resist. Results of the simulation work have aided in a better understanding on the differences in imaging characteristics of e-beam resists and DUV or other optical-based resists. For example, the exposure process for 45 nm contact hole arrays was simulated and compared to experimental results obtained using a 100 KV JEOL JBX-9300FS DW tool, showing excellent agreement. The simulation work provided detailed information on ionization statistics and photoacid generation due to exposure to high-energy electrons. Ionization statistics show that most of the secondaries generated in the resist have energies well below 100 eV, peaking at around 10 eV. At these low energies impact ionization or plasmon generation are not possible, which means other types of interactions between secondary electrons and PAG come into play for photo-acid generation.

9:00 AM *Y1.2

FULLERENE NANOCOMPOSITE RESIST FOR 100-KV ELECTRON-BEAM NANOPATTERNING. Tetsuyoshi Ishii, NTT, Photonics Labs, Atsugi, Kanagawa, JAPAN; Yuka Murata, Tokyo Univ of Agriculture and Technology, Dept of Applied Chemistry, Tokyo, JAPAN; Kiyotaka Shigehara, Tokyo Univ of Agriculture and Technology, Dept of Applied Chemistry, Tokyo, JAPAN.

Electron-beam lithography (EBL) is widely employed for the research and development of next-generation LSIs and novel innovative devices. In order to improve the resolution in EBL, it is essential to apply a thinner resist film to minimize the scattering effects of electrons. We have developed a nanocomposite resist system that incorporates fullerene molecules (C60 and/or C70) into a positive-type electron beam resist, ZEP520 and demonstrated a resolution improvement by using an ultrathin film that is made possible by enhanced etching resistance. In addition to resist thinning, the general trend has been to use a higher acceleration voltage for increased beam resolution as well as decreased scattering effects. Several exposure tools with an acceleration voltage of 100 kV are currently available on a practical

basis. The combination of fullerene nanocomposite resist and a 100-kV tool has the potential to further improve the resolution and will extend EBL versatility in nanolithography. In this paper, the 100-kV exposure characteristics of nanocomposite ZEP are examined for various nanodevice fabrications. Employing the unique characteristics of fullerene nanocomposite resist, i. e., that sensitivity can be readily changed with fullerene content due to the dissolution inhibiting effect of fullerene, we constructed a bilayer resist system for lift-off comprising a fullerene-incorporated ZEP top layer and a pure ZEP bottom layer. Some examples of densely packed nanodot patterns fabricated by the bilayer system exposed with a 100-kV beam will be presented. Fullerene-derivative nanocomposite systems have shown better sensitivity characteristics due to the enhanced solubility of the derivatives. The sensitivity of the systems can be significantly improved by using a derivative with multi-functional groups. Some advanced fullerene nanocomposite systems will be discussed.

9:30 AM *Y1.3

CHEMICALLY AMPLIFIED RESIST APPROACHES FOR E-BEAM LITHOGRAPHY MASK FABRICATION. J.R. Maldonado, Z. Tan, Etec Systems, Inc., and Applied Materials company, Hayward, CA; M. Angelopoulos, IBM T.J. Watson Research Center, Yorktown Heights, NY; R. Brainard, Shipley, Marlborough, MA.

This paper describes several e-beam resist systems utilizing chemical amplification suitable for mask fabrication for device generations below 100 nm. The challenges of mask fabrication for future device generations will be presented together with the stringent resist requirements. In particular, three resist systems developed specifically for mask fabrication will be described: a Si-doped version of the IBM KRS-XE resist (now commercially available) developed at IBM Research; a modified ESCAP resist with enhanced properties developed at Shipley; and a new MANA resist also developed at Shipley. Chemically amplified resists for mask making on glass plates require better PEB latitude than resists utilized for device fabrication on wafers. This is due to the different thermal properties of the resist substrate. Relatively thick glass plates are very difficult to heat uniformly, and thermal time constants play a much larger roll in the resist development characteristics compared to high thermal conductivity thin silicon wafers. The etching properties, PEB latitude, shelf life stability and outgassing properties of the newly developed resist will be presented and compared with common resists. Some of the resist properties are summarized in the table below. Resist Parameter IBM/KRS-Si (New) Shipley 9947A (New) MANA (New) Sensitivity ($\mu\text{C}/\text{cm}^2$) @50 Kv 3.5 8.4 17 Resolution (nm) <100 90-80 (dense and iso) 100-80 Aspect Ratio >3:1 4 3.9 Dry etch resistance 1.2 nm/sec-20%. Better than Novolak Experiments in progress Experiments in progress Contrast >10 18:1 >10:1 Exposure Latitude >20% >25% TBD PEB Sensitivity nm/C PEB not required <1 Excellent Coated Shelf life 3 months (sealed) >3 months TBD Commercialization Very likely after KRS-XE becomes available TBD This is the first time this kind of resist was developed An important issue to be discussed is the difficulty of commercializing a new e-beam resist suitable for mask fabrication. This is mainly due to the relatively small volumes required when compared to resists suitable for optical lithography device making.

This work was partially supported by a DARPA/SPAWAR contract with Etec Systems (an Applied Materials Company). IBM Corporation and Shipley were subcontractors to Etec Systems under DARPA/SPAWAR contract No. N66001-9138-8485.

10:30 AM *Y1.4

THE ROLE OF FLUOROPOLYMERS IN NEXT GENERATION LITHOGRAPHY. Christopher K.Ober, Young Bae, Dirk Schmaljohann, Victor Pham, Gina Weibel, Cornell University, Dept of Materials Science & Engineering, Ithaca, NY; Willard Conley, International Sematech, Austin, TX; Karen Gleason, Hilton Pryce-Lewis, MIT, Dept of Chemical Engineering, Cambridge, MA.

Fluoropolymers, materials long ignored as photoresists, have recently become very interesting as possible lithographic materials because of their unusual transparency and low dielectric constant properties. This presentation will first overview our recent efforts in the design and synthesis of 157 nm resists. Base soluble copolymers of fluorocarbonyl containing polymers have been shown to have transparency at 157 nm and can be patterned using chemically amplified resist strategies to sub-100 nm dimensions. The properties of these and related aqueous base soluble polymers and their syntheses will be described. If the fluorine density is increased, an extremely non-polar, insulating material can be produced. As the second part of this presentation, CVD deposited fluoropolymers and their development using supercritical CO₂ will be described. Images as small as 100 nm have been produced using this technique. The enabling features and the environmental aspects of this work will be described. The authors wish to thank the Semiconductor Research Corporation, the National Science Foundation, Intel and International Sematech for financial

support. The use of the facilities of International Sematech and the Cornell Nanofabrication Facility are also appreciated.

11:00 AM *Y1.5

CONFINEMENT EFFECTS ON ACID TRANSPORT IN ULTRATHIN CHEMICALLY AMPLIFIED PHOTORESISTS.

Dario L. Goldfarb, Marie Angelopoulos, IBM T.J. Watson Research Center, Advanced Lithography Materials and Processes, Yorktown Heights, NY; Brian Trinqué, Sean D. Burns, C. Grant Willson, Univ. of Texas, Depts. of Chemistry and Chemical Engineering, Austin, TX; Eric K. Lin, Ronald L. Jones, Christopher L. Soles, Joseph L. Lenhart and Wen-li Wu, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD.

In the next few years, the resolution limits for the deep UV photolithographic processes widely used in the microelectronics industry must be extended to sub-100 nm length scales to keep pace with the persistent demand to write increasingly smaller device features. However, sub-100 nm lithography poses several potential difficulties that have yet to be addressed adequately. For example, device dimensions below 100 nm will require critical dimension controls of 10 nm or better, approximately the same size of the macromolecules used in photolithography, and it is unclear whether such a fine level of control can be achieved. Furthermore, the optical solutions for sub-100 nm lithography, including 157 nm excimer lasers and EUV radiation sources, are strongly absorbed by most polymer films. At these wavelengths the overall film thickness needs to be 100 nm or less for uniform illumination throughout the film thickness. Under these conditions the polymers are highly confined by the two dimensionality of the thin film geometry and deviations in material properties, such as the glass transition temperature, viscosity, transport kinetics, etc., are likely. In this work, bilayers of isotopically labeled protected and deprotected chemically amplified photoresists create a two-dimensional model of the line edge in a lithographic feature. X-ray and neutron reflectivity are used to quantify the spatial and temporal (kinetics) characteristics of the photogenerated acid diffusion and the resulting deprotection at the buried interface as a function of confinement (film thickness) and the baking temperature. The spatial extent of reaction in the buried interface is then correlated with the resulting roughness and the change in film thickness that occurs upon developing the exposed film, indicative of the critical dimension control achievable in highly confined photoresist films.

SESSION Y2: ADVANCED MATERIALS AND PROCESSES FOR NANOLITHOGRAPHY II

Chairs: Marie Angelopoulos and Lhadi Merhari
Monday Afternoon, November 26, 2001
Back Bay D (Sheraton)

1:30 PM *Y2.1

PREDICTING IMAGE PLACEMENT DISTORTIONS INDUCED DURING NANOPATTERNING.

Roxann L. Engelstad, Edward G. Lovell, Phillip L. Reu, Computational Mechanics Center, University of Wisconsin, Madison, WI.

Advanced lithographic technologies face a difficult challenge in order to meet the stringent overlay requirements for sub-100 nm lithography. Extending 157 nm lithography to the 70 nm node will require innovative technical approaches. In addition, it may be necessary to accelerate research and development of Next-Generation Lithography (NGL) alternatives to meet the expectations of the International Technology Roadmap for Semiconductors. A key issue for both optical lithography and the NGL technologies is the design and implementation of low-distortion masks. Research at the University of Wisconsin Computational Mechanics Center is addressing the development of advanced lithographic masks for the sub-100 nm regime. Finite element (FE) modeling and simulation is being used to investigate materials, fabrication processing and general system parameters to achieve the necessary pattern placement accuracy. This paper presents results on a comparison study of continuous membrane versus stencil membrane formats for the fabrication of Electron-beam Projection Lithography (EPL) masks. To illustrate the influence of feature density gradients on pattern transfer distortions, two typical mask patterns were employed: (a) an interconnect layer from an SRAM design, which is a repeating orthotropic-like layout, and (b) a sparse pattern, which simulates the contact layer of the same design. Equivalent modeling techniques were used to simulate the characteristics of the nanopatterns. A test layout of SRAM, sparse, and half-and-half patterns (within individual windows on the mask) was setup to identify the effects of pattern density gradients on the response of the two EPL formats. The FE data agreed exceptionally well with the experimental image placement measurements taken at the NGL Mask Center of Competency. In essence, the maximum in-plane distortions coincided with the windows having the highest pattern density gradients and the largest free span configuration. The

results emphasize the benefits of the modeling and simulation programs for design and optimization before implementation.

2:00 PM *Y2.2

NANOLINE FORMATION BY USING SMALL AGGREGATE RESIST AND SUPERCRITICAL RESIST DRYING.

Hideo Namatsu, NTT Basic Research Laboratories, Kanagawa, JAPAN.

In sub-10-nm lithography, the linewidth accuracy as well as resolution becomes important factors. This is because the amount of linewidth fluctuation or line-edge roughness (LER) cannot be disregarded as the linewidth decreases. Therefore, resist materials satisfying resolution and linewidth accuracy have to be used for nanolithography. In addition, there is a problem of pattern collapse in obtaining nanolines. The patterns tend to collapse when nanometer sized lines are formed. The solution of the pattern collapse, therefore, is one of the important issues for nanopatterning. In this paper, a resist material providing high resolution and small linewidth fluctuation is reported. In addition, supercritical resist drying (SRD) is described to solve the pattern collapse. Polymer aggregates, which are generally contained in resist films, cause LER. This is because the aggregates that remain on the pattern sidewall result in the roughness. The problem can be solved by using a small aggregate resist. A typical example is hydrogen silsesquioxane resist, HSQ. This is because HSQ has a rigid three-dimensional network, which does not spread out in the solution. The prevention of the spreading out shows the fact that the aggregate size of HSQ is much smaller than that of conventional e-beam resists. On the other hand, SRD is a powerful method for preventing pattern collapse, because the supercritical fluid eliminates the effects of the rinse solution; the surface tension of the rinse solution remaining between the dense lines, or the swelling of the rinse solution remaining in the isolated lines. Therefore, the resolution can be improved by using the SRD technique. The application of HSQ and SRD to nanolithography leads to the formation of a nanoline with enough height for etching masks. As a result, HSQ patterns with less than 10 nm widths and less than 1 nm LER can be formed without any collapse.

2:30 PM Y2.3

HIGH-SENSITIVITY RESISTS PREPARED FROM A PHOTOACID GENERATING MONOMER.

Kenneth E. Gonsalves, Dept of Chemistry, Univ of North Carolina, Charlotte, NC; Hengpeng Wu, Clariant Corporation, Somerville, NJ.

A photoacid generating (PAG) sulfonium monomer was designed and synthesized. The PAG homopolymer was sensitive to both UV as well as electron radiation and therefore acted as a high sensitivity negative resist without utilizing chemical amplification (CA). The PAG/methacrylate copolymers also functioned as novel chemically amplified resists with PAGs incorporated in the polymer chain. Due to the absence of phase separation, high PAG loading was realized, resulting in enhanced sensitivity CA resists. These resist proved to be especially useful for low-voltage EB lithography.

3:15 PM *Y2.4

ALL CO₂-PROCESSED FLUOROPOLYMER-CONTAINING PHOTORESIST SYSTEMS.

Joseph M. DeSimone, Christopher L. McAdams, Devin Flowers, University of North Carolina, Dept of Chemistry, Chapel Hill, NC; Erik N. Hoggan, Ruben G. Carbonell, North Carolina State University, Dept of Chemical Engineering, Raleigh, NC.

We present our progress on the development of completely CO₂-processed photoresists. Our partially fluorinated polymers and PAGs allow for the deposition, development and removal of photoresists using only liquid and supercritical CO₂. These photoresists function on the basis of a photochemically induced change in the dissolution rate of the polymer film in CO₂. By taking advantage of the unique tunable solvating properties of CO₂, we can adjust the solvent to give a kinetically controlled dissolution process. We demonstrate a rational basis for the future design of materials for use with special equipment that would allow for completely CO₂-processed systems.

3:45 PM *Y2.5

POLYXOMETALLATE CONTAINING POLYMERIC MATERIALS FOR NANOLITHOGRAPHY AND MOLECULAR DEVICES.

Nikos Glezos, Panagiotis Argitis, Dimitris Velessiotis, Panagiotis Koutsoulelos, Konstantinos D. Diakoumakos, Angeliki Tserepi, Institute of Microelectronics, Konstantinos Beltsios, Institute of Physical Chemistry, NCSR Demokritos, Aghia Paraskevi, GREECE.

In this paper, molecular compounds that come from the class of tungsten or molybdenum polyoxometallates (POM) are examined as components of polymeric materials with potential use in nanolithography and molecular devices. In the past, POMs have been used as components of DUV resists with promising results, but the

metallic compound presence and their unconventional processing demands discouraged their further use in microlithography. In this paper routes for the use of these compounds in e-beam nanolithography and possibly in mask fabrication are evaluated. Different resist formulations, where poly (vinyl alcohol) and poly (methyl methacrylate) are used as host polymers will be discussed along with the related process issues. First results from the use of polyoxometallate compounds as active elements, or components, of molecular electronic nanodevices will be also presented. The main reason for selecting molecules of this class is their well defined and stable structure as well as their thermal or photochemical reduction-oxidation, and catalytic properties. Due to their structural resemblance to semiconductor materials these compounds can be considered as zero dimension semiconductors. The electronic transport properties of the composite materials have been tested using planar devices with contact distances of 40m, 5m, 50nm and 25nm. Contacts were fabricated using electron beam lithography and a lift-off process. Even at room temperature conditions conductivity peaks appear in the case of distances smaller than 25nm. These peaks are related to the energy distance of the HOMO - LUMO levels of the active molecules and the work function of the electrode used. The position and the size of the peaks depends upon the mean distance of the molecules as well as the electrode distance. On the other hand when the contact is illuminated, conductivity increases even by two orders of magnitude. This is attributed to the photon excitation of electrons from the HOMO.

4:15 PM *Y2.6

NOVEL APPROACHES TO NANOPATTERNING: FROM SURFACE MONOLAYER INITIATED POLYMERIZATION TO HYBRID ORGANOMETALLIC-ORGANIC BILAYERS.

Clifford L. Henderson, Sean Barstow, Augustin Jeyakumar, Kendra McCoy, Dennis W. Hess, Georgia Institute of Technology, School of Chemical Engineering, Atlanta, GA; Laren M. Tolbert, Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA.

The extendability of conventional subtractive lithographic processing using spin-coated polymeric resists faces many challenges as feature sizes in microelectronics push below 100 nm. In addition, the opacity of polymeric materials to future exposure sources presents new challenges as the radiation penetration depth decreases (e.g. 157nm, EUV, low keV e-beam). One solution to these problems is the use of so-called top surface imaging (TSI) methods in which exposure in only a thin surface layer is used to create a pattern in a much thicker etch barrier layer. Conventional TSI approaches have mainly involved the use of silylation, which have seen little industrial use due to a variety of associated problems. This presentation will focus on our work to explore the concept of TSI using novel imaging material systems and strategies. First, results of our work on surface monolayer initiated polymerization (SMIP) will be discussed. The basic idea in SMIP is to extend the idea of TSI near its limits, i.e. where the initial image or pattern is defined in a monolayer. In this method (1) a pattern is first defined by radiation exposure of a reactive monolayer whereby exposure deactivates selected areas of the monolayer, and (2) subsequently the remaining areas can be activated to generate radicals (or other initiator sites) that are used to amplify the initial pattern by growth of an etch resistant polymer. This method is extremely flexible and also shows significant promise in the fabrication of sensors and biological devices. Second, we have been exploring the use of a novel bilayer imaging system based upon a conventional organic polymer underlayer in conjunction with a novel patternable organometallic imaging layer. Exposure of the organometallic layer to radiation locally converts the film to an etch resistant metal oxide while the unconverted film can be developed away.

SESSION Y3: NEXT-GENERATION AND EMERGING LITHOGRAPHIES

Chairs: Daniel J. C. Herr and Lhadi Merhari
Tuesday Morning, November 27, 2001
Back Bay D (Sheraton)

8:30 AM *Y3.1

EXTREME ULTRAVIOLET LITHOGRAPHY: PROGRAM OVERVIEW AND MATERIALS CHALLENGES.

Donald W. Sweeney, Lawrence Livermore National Laboratory, Livermore, CA.

Extreme Ultraviolet Lithography (EUVL) is a leading candidate for the next generation of high-volume lithography. A number of technical accomplishments during the past year have substantially improved the expectation that EUVL will be the primary critical-layer lithography at the 50nm Critical Dimension (CD) node and beyond. Most significantly, a full-field, alpha-class lithography tool called the Engineering Test Stand (ETS) has been operational since March,

2001. The 0.1 numerical aperture optical system currently installed in the ETS produces 25mm x 32mm wafer images with 100nm resolution with limited capability at 70nm resolution. An optical system with superior surface quality will be installed in the ETS this Fall; the new optical system has already demonstrated static imaging with 70nm resolution at the Advanced Light Source at Lawrence Berkeley National Laboratory. The basic parameters of the ETS and the latest imaging results will be presented. EUVL is conceptually identical to current optical lithography with the notable distinction of using the soft x-ray wavelength of 13nm. Lithography-quality imaging at 13nm requires that all optical surfaces be multilayer-coated reflectors. These highly reflective, atomic-precision multilayer coatings are the enabling technology for EUVL. Optical systems have been coated with profile control at the picometer level. The goal is to produce multilayers with greater than 70% reflectivity and lifetimes in the lithographic tool of greater than five years. The EUVL mask is also reflective. The mask multilayer must be defect free over its entire area. Defects as small as 50nm lateral extent and 2nm high can be critical defects on the mask. Substantial progress has been made in defect reduction during the last year. Totally new approaches have been developed for multilayer defect repair. The latest results in defect-free masks will be presented.

9:00 AM *Y3.2

EXTREME ULTRAVIOLET LITHOGRAPHY: PATTERNING TO THE END OF THE ROAD. Jonathan Cobb, Motorola, Inc., Austin, TX.

Extreme Ultraviolet Lithography (EUVL) is gaining momentum as the Ultralarge-Scale Integration patterning technology of choice for the 50-70 nm nodes and below of the SIA roadmap. As such, it must be ready for manufacturing in the 2005-2007 time frame, and it must be extendable to the lower limits of CMOS technology. In addition to the apparent resolution, dimension control, and process control requirements, EUVL patterning presents further unique challenges due to the short wavelength of the radiation (13-14 nm). First, since all photoresist materials absorb these wavelengths strongly, the imaging layer must be less than 150 nm thick, which is several times thinner than the photoresist layers used in today's leading-edge technologies. Thus, techniques to apply these thin coatings without defects and to transfer the exposed resist patterns into the underlying device layers must be developed. Second, since EUV photons are difficult to create, the photoresist must use them efficiently. Wafer throughput models indicate that patterning doses may need to be less than 4-5 mJ/cm², and only 30-40% of these photons will be absorbed, so the resists must be able to accommodate statistical dose fluctuations that are an appreciable fraction of the mean dose. Third, although little is understood about the impact of line-edge roughness (LER) on device performance, it is generally assumed that LER must be less than 4 nm 3σ. Fourth, EUV resists must be stable in vacuum, and they must not outgas contaminants upon exposure that are beyond the levels the environmental system can control. Efforts are well underway in the United States, Europe, and Japan to address all of these issues, and the progress that has been made and the current level of understanding will form the bulk of the presentation.

9:30 AM *Y3.3

EXTENSIBILITY OF PROXIMITY XRL: ROADMAP FOR 35 NM AND BEYOND. F. Cerrina, Electrical and Computer Engineering & Center for Nanotechnology, University of Wisconsin, Madison, WI.

Proximity X-ray Lithography has a long development history, but never quite made it in the mainstream of semiconductor lithography. It is possible that this is because the goals were set for unrealistically close targets – always the “next node”. If we ask the question of “how small can we pattern using XRL” and disconnect ourselves from the beaten paths of the SIA Roadmap, several interesting possibilities for nanopatterning become possible. Hence, we will review aggressive mask design and exposure optimization for general nanopatterning at 35nm and below, showing that (on the basis of rigorous physical analysis) it is possible to extend PXL in the deep nanolithography regime.

10:30 AM *Y3.4

RESISTLESS PATTERNING OF MAGNETIC STORAGE MEDIA USING AN ION BEAM PROJECTION TECHNIQUE. R. Berger, H. Grimm, A. Dietzel, IBM Deutschland Speichersysteme GmbH, Mainz, GERMANY; W.H. Bruenger, C. Dzionk, Fraunhofer Institute of Silicon Technology, Itzehoe, GERMANY; F. Letzkus, R. Springer, IMS Chips, Stuttgart, GERMANY; H. Loeschner, E. Platzgummer, IMS GmbH, Vienna, AUSTRIA; S. Anders, Z. Bandic, C.T. Rettner, B.D. Terris, IBM Almaden Research Center, San Jose, CA.

The rapid increase of areal storage densities in magnetic hard disk drives may in the future be limited by the thermal instability of small magnetic domains which is known as superparamagnetism. A patterned storage media featuring independent single magnetic domain bit cells would allow to further postpone this limitation. Ion

beam projection (IBP) techniques facilitate a resistless structuring process which is attractive for manufacturing of future magnetic storage media. A complex pattern including data and servo information can be transferred into the magnetic media. Such specific structures can be already defined in a stencil mask which allows mass replication. One advantage of the IBP technique is that the complex pattern in the stencil mask can be transferred into the magnetic medium at a given demagnification factor (e.g. 8 x), which simplifies the stencil mask process. Stencil mask patterns may have either rotational or translational symmetry. Experiments are presented where CoPt multilayer media with strong perpendicular anisotropy are magnetically altered in areas of local ion beam interaction. Hereby the topography of the media is preserved in contrast to other patterned media approaches. We report the influence of different ion species and ion doses on magnetic parameters of irradiated samples. Simulations of different ion doses and energies show the intermixing of Co and Pt layers in the sample and allow to predict magnetic coercivity changes in dependence of the ion doses. The latter value determines the exposure time for a manufacturing process. An IBP tool which is currently developed within an European consortium (MEDEA) for next generation lithography will be used to evaluate a manufacturing process for magnetic storage media. This tool allows to irradiate samples up to a diameter of 17 mm with a single exposure.

11:00 AM *Y3.5

LITHOGRAPHIC PERFORMANCE OF ION PROJECTION.

Wilhelm H. Bruenger, Fraunhofer Institute for Silicon Technology, ISiT, Itzehoe, GERMANY.

As part of the European MEDEA project on Ion Projection Lithography (IPL), headed by Infineon Technologies, a process development tool has been assembled at IMS, Vienna. Recent results of the exposure tests which are now being conducted will be presented. Parallel work continued at the experimental ion projector of the Fraunhofer Institute ISiT. New open stencil masks produced by IMS-Chips, Stuttgart, with smaller feature sizes and aspect ratios up to 6 have been irradiated with light (He+) and heavy (Ar+) ions for stability tests. Ion exposures of nanocomposite resists consisting of commercial chemically amplified and non amplified resists with dispersed surface treated silica nanoparticles showed no degradation of the radiation sensitivity. The aim is improved etch resistivity and stability against pattern collapse of high aspect ratio features. The high resist sensitivity below 1 micro C/cm² for 75 keV He ions and the absence of a proximity effect make ion projection a promising candidate for Next Generation Lithography.

11:30 AM Y3.6

PLASMON PRINTING: A NEW APPROACH TO NEAR FIELD LITHOGRAPHY. Pieter G. Kik, Stefan A. Maier, and Harry A. Atwater, California Inst of Tech, Dept of Applied Physics, Pasadena, CA.

The minimum feature size that can be obtained using projection lithography is determined by the diffraction limit. We propose a new approach to lithography that could enable the printing of sub-wavelength patterns.

The proposed method relies on the plasmon resonance occurring in nanoscale metallic particles. Gold nanoparticles (diam. < 100 nm) exhibit a collective electron oscillation (surface plasmon) when illuminated with visible light. In air this plasmon excitation occurs resonantly at a wavelength of ~480 nm, producing a strongly enhanced electromagnetic field near the particle. We propose to use this enhanced near field to locally expose a thin layer of resist. This method could enable the generation of sub-wavelength replicas of nanoparticle arrays in a parallel fashion, using broad beam illumination with visible light.

The applicability of the proposed scheme depends on the magnitude of the field enhancement and the exact time-dependent field distribution around the metal nanoparticles. Finite difference time domain (FDTD) calculations on 50 nm diameter gold particles in contact with a 100 nm thick layer of photoresist reveal a clear intensity enhancement in the resist just below the particle under illumination at a wavelength of ~600 nm. The lateral extent of the area showing enhanced intensity is 25 nm (less than 5 % of the wavelength), illustrating the potential for producing high-resolution patterns. The maximum intensity enhancement occurs at a depth of 16 nm below the particle, and amounts to a factor 15. Optimum illumination wavelengths for a number of metals as well as constraints on resist thickness and substrate composition will be discussed, along with experimental results obtained using an Ar laser and commercially available photoresist.

11:45 AM Y3.7

OPTICAL NANOLITHOGRAPHY ON AZO-HYBRID GELS, THE NEAR-FIELD APPROACH. Nathalie Landraud, Frederic Chaput, Jacques Peretti, Khalid Lahli, Jean-Pierre Boilot, Georges Lampel, Viatcheslave Safarov, LPMC, CNRS-Ecole Polytechnique, FRANCE.

Scanning near-field optical microscopy has been developed to overcome the diffraction limit of conventional optical methods and combines the potentials of scanned probe technology with the power of optical microscopy. One of the very attractive applications we have developed in our laboratory is the local modification of the physical properties of the studied materials. We report here on the photo-fabrication and characterization of topographic nanometric features on azobenzene functionalized sol-gel thin film. A combined scanning near-field optical microscope and shear-force microscope has been utilized. Using tapered optical fibers to irradiate our samples, we can address a region whose size depends on the aperture at the tip of the probe as well as the tip-film surface separation. After irradiation (568nm), shear-force imaging reveals protuberances with lateral dimensions as small as 50nm. Photolithography on the nanometer scale and high-density optical data storage are promising applications of these experiments.

SESSION Y4: NANOFABRICATION WITH CHARGED PARTICLE BEAMS

Chairs: Marie-Isabelle Baraton and Daniel J. C. Herr
Tuesday Afternoon, November 27, 2001
Back Bay D (Sheraton)

1:45 PM *Y4.1

FOCUSED ION BEAM FABRICATION OF PHOTONIC

NANOSTRUCTURES. A.J. Steckl, R. Chi, B. Lee, I. Chyr, J. Cheng, and F. Beyette, University of Cincinnati, Nanoelectronics Lab, Cincinnati, OH.

Focused ion beam systems provide a unique device fabrication capability by being able to customize the process on a scale comparable to the ion beam parameter (<100 nm). This is particularly important for the integration of photonic devices where the presence of a large variety of materials and 3-D structures make conventional planar batch processing difficult. In this paper we review several photonic devices and applications implemented with FIB nanofabrication: optical memory storage, optical waveguides, diffraction gratings. For example, high density optical memory devices have been fabricated by two bit 'writing' approaches: FIB Er-implantation into GaN and Ga⁺ FIB milling of SiO₂/Si. In the former approach, the memory 'read' process is based on upconversion emission from Er 'bits'. Reading of the pattern is performed with near-infrared lasers (at 840 or 1000 nm) resulting in visible green emission (at 522 and 546 nm). 2-D memory devices have shown a storage density of 10⁸ bits/cm², while extension of this approach to 3-D could produce very high densities (~ 10¹² bit/cm³). In the latter memory approach, we utilize FIB milled regions of varying thickness to adjust the spectral characteristic of reflected light from a broad band source. This digital thin-film (DTF) color optical memory has been implemented in structures with 16 physical levels or 4 bits/pixels providing an equivalent storage density of ~ 10⁹ bits/cm², with potential extension to 10¹¹ - 10¹² bits/cm². We will also review the implementation of novel rare-earth (Er, Pr) sources required for the fabrication of certain memory and light emitting devices, the use of gas-assisted (XeF₂, I₂) used to enhance the FIB milling process for waveguide fabrication and provide some speculation on future directions of FIB fabrication of photonic nanostructures.

2:15 PM Y4.2

ION BEAM SCULPTING ON THE NANOSCALE. Derek Stein, Jiali Li, Michael J. Aziz, Division of Engineering and Applied Science, Harvard University, Cambridge, MA; Daniel Branton, Department of Molecular and Cellular Biology, Harvard University, Cambridge, MA; J.A. Golovchenko, DEAS and Department of Physics, Harvard University, Cambridge, MA.

We report on the ability to controllably transform materials on the single nanometer length scale using low energy ion beams. In addition to removing matter from the surface by a sputtering process, low energy ion beam exposure stimulates significant surface atomic transport. These processes can be utilized to fabricate solid state structures and devices with single digit nanometer control in a variety of geometries and materials using a feedback controlled ion beam sculpting apparatus. Our experiments focus on ion beam sculpting nanopores in thin insulating membranes and reveal the dynamical nanoscale atomic transport phenomena in a quantitative manner. The results are consistent with an "adatom" surface diffusion model and they yield parameters needed to apply the method to nanoscale device fabrication. As an application we demonstrate an electronic solid state single molecule detector, fabricated by ion beam sculpting, that operates in an aqueous environment.

2:30 PM Y4.3

NANOSCALE ELECTROCHEMICAL DEPOSITION OF METALS

ON FIB SENSITIZED P-TYPE SILICON. Adrian Spiegel, Swiss Federal Inst of Tech-Lausanne (EPFL), Dept of Matls Sci, LTP, Lausanne, SWITZERLAND; Patrik Schmuki, Dept. of Matl Sci, LKO, Univ of Erlangen-Nuremberg, Erlangen, GERMANY.

Focused Ion Beams (FIB) have been widely used as a tool for TEM sample preparation as well as for other micromachining applications. Also, direct deposition/implantation of material onto Si surfaces has been performed. While FIB offers an exceptional spatial resolution for these applications, its widespread use has been hindered by the comparatively long exposure times needed for any substantial milling/implantation to occur. This work reports the use of FIB to produce local damage sites on the surface of p-Si that lead to the modification of the semiconductor/electrolyte interface behaviour. Subsequent electrochemical treatment of the Si wafer results in selective deposition of metallic species present in the electrolyte (Cu, Au, and Pd) at the defect sites. The nature of surface modifications of the Si sample due to FIB bombardment as well as mechanistic aspects of the electrochemical metal deposition has been studied as a function of ion implantation dose, electrolyte, applied cathodic potential and length of the electrochemical treatment and a range of techniques (SEM, AFM, AES) were used for characterization. We show that maskless deposition of metallic patterns of arbitrary shapes is possible in the sub-micrometer range. Only very short beam exposition times (in the order of milliseconds) are needed as the electrochemical process is extremely sensitive to surface modifications which could make this process suitable for larger scale applications.

2:45 PM Y4.4

RAPID PATTERN DIRECT WRITING AND PATTERN TRANSFER USING FIB - FABRICATED MASTERS FOR MICROCONTACT PRINTING. Yajing Liu, David M. Longo and Robert Hull, Univ. of Virginia, Dept of Materials Science and Engineering, Charlottesville, VA.

We have employed focused ion beam (FIB) fabrication of topographic masters for microcontact printing. The advantages of this technique are high depth of focus ($> 100 \mu\text{m}$ while maintaining sub-100 nm resolution), rapid prototyping capabilities (fabrication requires neither mask nor resist), and the ability to efficiently and directly modify or repair defects in the master. The primary limitation is throughput, with feature writing at maximum rates of order $10^1 - 10^2/\text{s}$ (for 100 nm size features) in inorganic materials such as Si, which can limit master arrays to approximately 10^6 features over a 1 mm^2 area for practical fabrication times. A new method is presented here that largely overcomes these throughput issues. It is found that a 30 keV Ga^+ FIB can create shallow nanoscale ($\sim 100 \text{ nm}$ in diameter) topographic patterns in polymeric materials, such as Polymethylmethacrylate (PMMA), at speeds up to 10^4 features/s. This is equivalent to sputtering yields of thousands of atoms per incident ion, orders of magnitude faster than encountered for other materials. This enables arrays of 10^4 features to be created over areas of order $(100 \mu\text{m})^2$ in seconds, potentially scaleable to areas of 1 cm^2 with 10^8 features in timeframes of order hours. The topographic FIB-patterned PMMA surface can be then used as a master from which elastomer replica molds are cast directly. Proof-of-concept microcontact printing results at resolution of order 100 nm into thin Ag films will be shown for this all-polymer process. The possible fundamental mechanisms behind this anomalously high sputtering yield in PMMA will be discussed.

3:30 PM *Y4.5

NANOFABRICATION AND ANALYSIS WITH ION AND ELECTRON BEAMS. P.E. Russell, A.R. Guichard, J. Wang, K.L. Bunker, J.C. Perez Gonzalas, and D.P. Griffis, Analytical Instrumentation Facility, North Carolina State University, Raleigh, NC.

Electron and ion beams are intimately involved in many aspects of nanotechnology, with applications ranging from nanopatterning to nanofabrication to nanocharacterization. While it can be said that electron and ion beams are enabling aspects of nanotechnology, nanofabrication needs are in fact driving the development of electron and ion beam techniques. A series of examples will be used in this paper to illustrate the close synergy between nanopatterning and electron/ion beam developments. Beam induced nanofabrication with 5 nm focused ion beam (FIB) systems is now commonly used for device and structure fabrication as well as for preparation on nm scale electron microscopy samples. Recently, chemically assisted FIB etching and deposition technologies have greatly extended nanofabrication capabilities while also reducing beam induced damage to nanopatterned structures. The developments toward next generation lithographies, especially deep UV and extreme UV, has driven the need to replace ion beam mask repair techniques with chemically assisted electron beam nanofabrication to avoid damage (or staining) of optical mask components (both transmissive and reflective). E-beams offer reduced spot size and reduced damage, but

with the lack of physical sputtering, require more sophisticated chemistries for etching of metals and dielectrics. Nanometer scale electron beams, particularly as Field Emission Scanning Transmission Electron Microscopy (FE-STEM) are providing nm level characterization of materials, device, and electrical properties. Examples of FE-STEM electron beam induced current (EBIC) combined with Z-contrast imaging and energy dispersive x-ray nanoanalysis used to characterize nm scale quantum well devices will be presented.

4:00 PM Y4.6

A VERSATILE APPROACH FOR BIOMATERIAL PATTERNING: MASKED ION BEAM LITHOGRAPHY. Kenneth Gonsalves, Dept of Chemistry, University of North Carolina, Charlotte, NC; Lhadi Merhari, CERAMEC R&D, Limoges, FRANCE; Wei He, Jim Koch, and Matthew Augustine, Institute of Materials Science, University of Connecticut, Storrs, CT.

Biomaterials play a key role in numerous medical applications ranging from tissue engineering to drug delivery systems. Surface micro-fabrication techniques have been widely utilized to improve the performance of biomaterials, including biopolymers. One of the most extensively investigated approaches is mechanical transfer of the micropatterns of a die into biopolymers. Although attractive, this approach has some intrinsic major shortcomings: (1) it is a two-step process including first generating the patterns on a die by standard lithographic methods, and then transferring the patterns into the polymer. This implies an unavoidable loss of fidelity and a lack of process reproducibility. (2) only the topography of the material can be modified leaving no possibility to specifically tailor the surface chemistry of the patterns. Therefore, as an alternative microfabrication method we employed MIBL (Masked Ion Beam Lithography) in our study. Since it is a one-step process, the patterns can be engraved into the polymer in a controlled manner. Moreover, by selecting the right ion to implant, such as K, Na, Ca, the surface chemistry of the biocompatible material can be tailored. In our preliminary study, Ca ion implanted PMMA was used as a model system. The patterns produced on the PMMA film were characterized using interferometry and AFM, while the profile of the implanted ions in the film was obtained by SIMS. The effects of the pattern geometry and implanted ion species as well, on the growth of certain cells will be further investigated.

4:15 PM Y4.7

FORMATION AND CONDUCTIVE PROPERTIES OF MINIATURIZED FULLERITE SENSORS. Alexander S. Berdinsky, Novosibirsk State Technical University, Novosibirsk, RUSSIA; Dietmar Fink, Manfred Müller, Alexander Petrov, HMI, Berlin, GERMANY; Lewis T. Chadderton, Australian National University, Canberra, AUSTRALIA; Pawel Yu. Apel, Flerov Laboratory of Nuclear Reactions, JINR, Dubna, RUSSIA.

Tracks of energetic ions in PET foils were etched, filled with C_{60} , and then electrically contacted on both sides of the foils. The resistivity of the ca. 200 nm wide and 10 μm long fullerite columns shows a pronounced temperature dependence. Whereas around ambient temperature the resistivity change is as large as ca. 1 order magnitude per 10°C , it becomes less dramatic at elevated temperatures. These C_{60} columns also exhibit a pronounced reproducible non-linear pressure dependence. We intend to develop now large-size arrays of these elements as light-weight flexible sensor fields with few μm lateral resolution. These devices are expected to be the first ones of a whole series of modularly built-up miniaturized elements of various functionalities (e.g. transformers, capacitors, transistors, ...) which are all hosted in etched ion tracks in polymers.

4:30 PM Y4.8

ION-SPUTTER INDUCED SPONTANEOUS NANOPATTERNING OF BULK AND THIN FILM OXIDES. Christopher C. Umbach, Kee-Chul Chang, Cornell Univ, Dept of Materials Science and Eng, Ithaca, NY; Randall L. Headrick, Univ of Vermont, Dept of Physics, Burlington, VT.

Sputtering by energetic ions in an off-normal incidence geometry can produce a large-area nanoscale periodic surface roughness without lithography; such patterns are attractive for enhancing metal film adhesion, orienting molecular thin-films, and growing nanoparticles. For example it has recently been demonstrated that off-normal sputtering with $\sim 200 \text{ eV}$ Ar ions can improve liquid crystal alignment in active-matrix displays (P. Chaudhari et al., Nature 411, 56 (2001)). We have studied the spontaneous formation of nanoscale corrugations arising from off-normal ion bombardment of glasses, bulk crystalline oxides and amorphous thin-film oxides. The corrugations on a thermally oxidized Si surface eroded by Ar ions have amplitudes of $\sim 1 \text{ nm}$, as determined by grazing incidence x-ray scattering and scanned probe microscopy. The corrugation wavelength λ^* depends almost linearly on ion energy between 0.5 and 2 keV, varying from 20 to 60

nm in this ion-energy range at room temperature. Between room temperature and ~ 200 C, λ^* depends weakly on temperature and above ~ 200 C it shows an Arrhenius-like increase. Ion-assisted viscous relaxation in a thin surface layer is shown to be the dominant smoothing process during erosion; the rate of viscous smoothing scales as $(\lambda^*)^{-4}$. Room temperature sputtering of a commercial liquid-crystal display glass (Corning Code 1737) results in a λ^* that is ~ 3 times that for the thermal oxide while λ^* for an evaporated SiO_2 film is ~ 1.5 times greater, suggesting that the large difference in intrinsic viscosity between these materials is not as important to corrugation formation as the ion-induced viscosity. Corrugations on crystalline Al_2O_3 exhibit a λ^* similar in magnitude to that observed for the glasses but possess a much greater degree of ordering. Feasibility experiments where corrugations in deposited oxide films act as etch masks for pattern transfer of the corrugation to underlying films will also be discussed.

4:45 PM Y4.9

TIME-RESOLVED X-RAY SCATTERING STUDY OF ION-INDUCED PATTERN FORMATION ON COBALT SURFACES. O. Malis, School of Applied and Engineering Physics, Cornell Univ., Ithaca, NY; R.L. Headrick, Cornell High Energy Synchrotron Source, Cornell Univ., Ithaca, NY; MinSu Yi, Kwang-Ju Institute of Science and Technology, KOREA; J.M. Pomeroy, Dept. of Physics, Cornell Univ., Ithaca, NY; J.D. Brock, School of Applied and Engineering Physics, Cornell Univ., Ithaca, NY.

Low-energy ion erosion of materials at low temperatures often results in the formation of surface ripples, mounds or pits with a narrow size distribution. This process is particularly interesting because it has the potential of being a novel technique to synthesize metallic and semiconductor dots at the nanometer scale. The exact morphology of the ion-induced self-assembled pattern depends on the material structure, ion energy, ion angle of incidence, and temperature. In spite of the extensive experimental and theoretical effort in the field, our understanding of the microscopic mechanisms governing sputtering is still limited. To gain insight into this process, we used *in situ* grazing incidence small angle x-ray scattering and Atomic Force Microscopy to investigate Ar ion sputtering of Co surfaces. Under ion irradiation at temperatures below 300°C , single crystal Co(0001) surfaces roughen and develop a pattern of mounds or pits. The average separation length between features, λ , increases with ion dose, ion energy and sample temperature. Taking advantage of the high flux x-ray source available at the Cornell High Energy Synchrotron Source, we studied in detail the real time evolution of this surface pattern. At early times the features coarsen following a power law $\lambda = A \cdot t^n$ with an exponent n lower than the predictions of recently proposed theoretical models and other experimental results. At later times, the coarsening law deviates significantly from a power law. In order to explore the microscopic processes occurring during ion erosion, Kinetic Monte Carlo simulations of sputtering were performed, and the results are compared with the experimental data. The simulations point to edge diffusion as the leading cause for mound formation during sputtering at low temperatures.

SESSION Y5: NANOSTRUCTURES AND NANOFABRICATION FOR BIOLOGICAL APPLICATIONS

Chairs: Ashutosh Chilkoti and Kenneth E. Gonsalves
Wednesday Morning, November 28, 2001
Back Bay D (Sheraton)

8:30 AM *Y5.1

NANOMETRIC PATTERNS FOR TISSUE ENGINEERING: FABRICATION AND IN VITRO BIOCOMPATIBILITY. M. Riehle¹, M. Dalby¹, H. Johnstone³, J. Gallagher¹, M.A. Wood¹, K. McGhee², B. Casey², S. Affrossman³, C.D.W. Wilkinson² and A.S.G. Curtis¹.
¹Centre for Cell Engineering, IBLs. ²Department of Electronic Engineering University of Glasgow, Glasgow, UNITED KINGDOM. ³Department of Pure and Applied Chemistry, University of Strathclyde, UNITED KINGDOM.

Three fundamentally different methods were used to fabricate nanometric surface features on polymers or fused silica. Phase separation of binary polymer mixes resulted in randomly distributed features whose depth and shape could be tightly controlled over large areas. Large areas were patterned by colloidal resist to give a locally random but overall uniformly pattern with very fine spikes. In contrast e-beam and reactive ion etching were used to create a set of regular spaced pillars on an orthogonal pattern. Some of the surfaces were replicated by *in situ* polymerisation, solvent casting, embossing or melt moulding onto PDMS, polystyrene (PS), η -polycaprolactone (η -PCL) and polyhydroxybutyrate (PHB). Nanometric features down to 60nm were imprinted onto some of the polymers (PDMS, PS, η -PCL) with high fidelity. Cells were seeded onto the nanometric

surfaces and adhesion, morphology and cytoskeleton investigated. Cells respond to regular features of 170/80nm (width/depth) with reduced adhesion and changes in overall morphology and cytoskeleton. Small nanofeatures (18nm, 45nm depth) made by phase separation on the other hand increased adhesion and promoted cytoskeletal differentiation. The responses of the cells are indicative that nanometric surface features are useful modifications on scaffolds for tissue engineering or for the surfaces of medical implants.

9:00 AM *Y5.2

MICROFABRICATION FOR CELLULAR ENGINEERING.

Mehmet Toner, PhD Center for Engineering in Medicine, Massachusetts General Hospital, Harvard Medical School, Boston, MA.

Biomedical application of microfabricated devices is no longer limited to non-living systems as genes-on-a-chip or lab-on-a-chip, recent advances in the understanding of cellular behavior in micro-environments have started to pave the way toward living micro-devices. These emerging devices are expected to become key technologies in the 21st century of medicine with a broad range of applications varying from diagnostic, tissue engineered products, cell-based high throughput drug screening tools, and basic molecular biology tools. They will also include multiple cell types and/or genetically engineered cells to investigate complex interactions between cells from different tissues. These sophisticated devices will contain micro-engineered tissue units coupled to each other by complex microfluidic handling network. Microfluidic mixing systems will also precisely regulate the composition and concentration of drugs to be tested. This presentation will focus on fundamental aspects of integrating cells into micro-devices. Special emphasis will be placed on cell-substrate and cell-cell interactions, and chemical and microfluidic approaches to control spatial distribution of cells on biocompatible surfaces. Next, several emerging areas of applications will be discussed including liver and skin tissue engineering using microfabrication, the use of dielectrophoresis to create cellular arrays for rapid screening, and microfluidic cellular chemotaxis assays.

9:30 AM Y5.3

E-BEAM PATTERNED POLY(ETHYLENE GLYCOL) FOR SPATIAL CONTROL OF SURFACE BIOACTIVITY. P. Krsko, C. Stuccio, M. Libera, Stevens Institute of Technology, Hoboken, NJ; and R. Clancy, Hospital for Joint Disease, New York University Medical School, NY, NY.

Poly(ethylene glycol) [PEG] has been used extensively in biomaterials applications to modify hydrophilicity. PEGylated surfaces typically exhibit reduced protein and cell adsorption. E-beam patterned PEG can be used to create biologically active surface features at length scales relevant to both proteins and cells. PEG thin films with thicknesses ranging from approximately 100 nm - 400 nm were spin coated onto silicon and glass substrates. Lithographic patterns with minimum feature sizes of order 100-200 nm were generated using a LEO 982 FEG Scanning Electron Microscope controlled externally by an Emispec Vision system. Electron-beam irradiation crosslinks PEG rendering it less soluble in a subsequent water rinse. As such, PEG can be used in much the same fashion as traditional e-beam photoresists. This research used electron doses ranging from 0.1 to 5 C/m² with electrons of 5-10 keV incident energy. The electron trajectories and energy-deposition profiles in the polymer thin films were modeled using Monte Carlo methods. The biophysical response was assessed using the cell binding fragment of human fibronectin (FN) together with a rabbit anti-FN primary antibody and either a goat anti-rabbit IgG FITC fluorescent secondary antibody or a 12 nm gold-labeled goat anti-rabbit IgG secondary antibody. Assessment using fluorescence optical microscopy or backscattered scanning electron microscopy shows that the patterned PEG features control the FN adsorption on either silicon or glass substrates. Work is ongoing to understand the effects of lithographically defined spatial constraints on the adhesion, proliferation and expression of specific cells in the context of biosensing and bioengineering applications.

9:45 AM Y5.4

THE DEVELOPMENT OF SURFACE ROUGHNESS AND IMPLICATIONS FOR CELLULAR ATTACHMENT IN BIOMEDICAL APPLICATIONS. Bruce Banks, Sharon Miller, Kim de Groh, NASA Glenn Research Center, Cleveland, OH; Amy Chan, Ohio Aerospace Institute, Cleveland, OH; Mandeep Sahota, Cleveland State University, Cleveland, OH.

The application of a microscopic surface texture produced by ion beam sputter texturing the surfaces of polymer implants has been shown to result in significant increases in cellular attachment as compared to smooth surface implants in animal studies. A collaborative program between NASA and the Cleveland Clinic Foundation has been established to evaluate the potential use of atomic oxygen texturing to improve osteoblast attachment to surfaces

that have been microscopically roughened. The range of surface textures that are feasible depends upon both the texturing process and the duration of treatment. To determine whether surface texture saturates or continues to increase with treatment duration, an effort was conducted to examine the development of such surface textures produced by various physical and chemical erosion processes. Both experimental tests and computational modeling were performed to explore the growth of surface texture with treatment time. Surface texturing by means of abrasive grit blasting of glass, stainless steel and polymethyl methacrylate was examined to measure the growth in roughness with grit blasting duration by surface profilometry measurements. Laboratory tests and computational modeling was also conducted to examine the development of surface roughening caused by directed and isotropic atomic oxygen attack of Kapton polyimide and Aclar (chlorotrifluoroethylene). For the atomic oxygen texturing tests, atomic force microscopy was used to measure the development of surface texture with atomic oxygen fluence. The results of all the tests and computational modeling support the premise that development of surface roughness obeys Poisson statistics. The results indicate that surface roughness does not saturate but increases as the square root of the treatment time.

10:30 AM *Y5.5

NANOPOROUS MICROFABRICATED MEMBRANES: FROM DIAGNOSTICS TO DRUG DELIVERY. Tejal Ashwin Desai, Univ of Illinois-Chicago, Chicago, IL.

Membrane-based biochemical separations are highly desirable for many biomedical applications ranging from biosensors to drug delivery. The ideal approach for implementing molecular size-based selectivity would be to design a synthetic membrane that has a collection of monodisperse nanopores, of molecular dimensions, that span the complete thickness of the membrane. These "molecular filters" could then be used to separate small molecules on the basis of size, for example, viruses and proteins during the blood fractionation process or the blocking of antibodies and complement molecules from encapsulated xenogeneic cells. However, pore sizes of <50nm have been difficult to achieve via normal lithographic processes. We have circumvented this limitation by using a combination of photolithography and deposition/selective removal of sacrificial layers, leading to silicon membranes with pore sizes down to several nanometers. The technology of micromachining can be used to create membranes with a multitude of pore configurations and arrangements, capable of high densities (>10⁹ pores/cm) and uniform pore sizes ($\pm 5\%$). In this presentation, we will describe the fabrication and application of photolithographically defined nanopore membranes consisting of arrays of parallel rectangular channels with precise dimensions in the 7-100 nm range. These membranes have been used to perform size based exclusion and controlled diffusion of model biomolecules. In addition to tightly controlled pore size distributions (<1% over a 4-inch wafer), these membranes take advantage of silicon's beneficial material properties such as biological, thermochemical, and mechanical stability.

11:00 AM *Y5.6

DESIGNING IN VITRO PATTERNED NEURONAL NETWORKS. Bruce C. Wheeler¹, Gregory J. Brewer², John C. Chang¹, Yoonkey Nam¹. ¹University of Illinois at Urbana-Champaign, Dept of Electrical and Computer Engineering Department and Beckman Institute, Urbana, IL. ²Southern Illinois University School of Medicine, Dept of Medical Microbiology, Springfield, IL.

Through the use of microstamped patterns of polylysine against covalently linked backgrounds of polyethylene glycol, we have been able to maintain patterns of neurons for up to a month in culture. We have demonstrated the ability to use patterning technology in combination with planar microelectrode arrays to confine the neurons to narrow (10 μ m or 40 μ m) tracks which intersect the electrodes and to record spontaneous electrical activity (action potentials) from them. Work is in progress to determine how sparse a network can be and still maintain functional electrical activity. This work is intended to provide a technological basis for robust, repeatable and designable neural networks from which one could study basic neuroscience or construct a neural biosensor. Supported by NIH grants R21 NS 38617-01 and R55 RR 13320-01 and fellowship F30 MH12897.

11:30 AM Y5.7

INTEGRITY OF PROTEIN MICROPATTERNS ON DEGRADABLE POLYMER SUBSTRATES. K.E. Schmalenberg and K.E. Uhrich, Dept of Chemistry, Rutgers University, Piscataway, NJ.

Repair of the peripheral nerve system is a complicated issue involving both topographic and chemical cues. When injury occurs to the nerve, regrowth of the affected cell must be directed along its original path for function to resume. Proteins that chemically enhance cellular attachment, such as laminin, were physically deposited to promote

neurite adhesion and outgrowth in a spatially specific manner. The micron-sized, protein-based patterns were created on polymeric substrates using microcontact printing, or soft lithography. Previous work focused on nerve cell outgrowth on poly(methyl methacrylate), whereas this study will focus on biodegradable polymer substrates including poly(hydroxybutyrate), poly(caprolactam) and poly(caprolactone). The protein micropatterns adherence as function of polymer degradation was primarily probed using nerve cells, although the physicochemical characteristics of the substrates will be evaluated by scanning electron microscopy and x-ray photoelectron spectroscopy.

11:45 AM Y5.8

RAPID THREE-DIMENSIONAL ARRAYING OF SINGLE CELLS. Vicki I. Chin, Mihrimah Ozkan, Sangeeta Bhatia, Univ of California, San Diego, Dept of Bioengineering, La Jolla, CA; Michael J. Sailor, Univ of California, San Diego, Dept of Chemistry, La Jolla, CA.

Arrays of mammalian cells on inorganic substrates have been used as a versatile tool in applications from biosensing to drug development. In particular, single cell arrays allow a large number of data points to be obtained on a limited, heterogenous cell population. We have developed electrophoretically patterned single cell arrays within fabricated microwells. This approach represents a significant advantage over both flow and scanning cytometry in its ability to gently isolate and recover cells of interest as well as its potential to easily automate image analysis. This system can also maintain arrayed cells in culture for analysis at multiple time points. Previous methods used to pattern cells usually require a time scale of hours in order for cells to preferentially localize to a chemical pattern; in this system, patterning is accomplished within minutes. Wells of fifteen micron diameter and twenty micron depth were etched into a silicon dioxide coated silicon substrate. The system was assembled with a transparent ITO counter-electrode to allow microscopic observation of the arraying process. A positive bias of 1-3 V was applied to the system, which electrophoretically drives negatively charged objects into the wells. Previous studies have shown that cells exposed to these low levels of applied voltages remain viable. We will present the application of this method to polystyrene beads as 'model cells' and live mammalian cells. Once arrayed, the cells should be confined within the wells, preventing migration over time. Data will be presented demonstrating the ability of this system to detect differential cellular characteristics using fluorescent biological assays.

SESSION Y6: FUNCTIONALIZATION AND ORDERING OF 1D AND 2D STRUCTURES

Chairs: Kenneth E. Gonsalves and Wilhelm H. Bruenger
Wednesday Afternoon, November 28, 2001
Back Bay D (Sheraton)

1:30 PM *Y6.1

SURFACE FUNCTIONALIZATION OF CERAMIC NANOPARTICLES: APPLICATION TO ION-SENSING AND GAS-SENSING DEVICES. Marie-Isabelle Baraton, UMR 6638 CNRS, University of Limoges, Limoges, FRANCE.

Tailoring the surface properties of nanosized ceramic particles is a challenging problem faced by scientists working in the fields of hybrid organic-inorganic nanocomposites (dispersion problems) and ceramic-based electronic transducers (selectivity and stability problems). We will review methods for grafting molecules like hydroxysilane, chlorosilane, and hexamethyldisilazane on various types of nanoparticles including Si₃N₄, Si₂N₂O, TiO₂, and SnO₂. FTIR spectrometry is used as primary investigation tool. In terms of physical properties modification, we will concentrate on the optimization of ion-sensitive FET and gas sensors. The beneficial effect of hydroxy- and chlorosilane grafted on Si₃N₄ and Si₂N₂O used as ion sensitive membranes will be demonstrated. Then the reduction of humidity effects on HMDS-grafted nanosized TiO₂ and SnO₂ powders used for screen-printed CO sensors will be reported. This work has been partially funded by the European Commission under the Brite-Euram and IST programmes.

2:00 PM *Y6.2

BIOSENSING AND BIOMOLECULAR PATTERNING USING NANOPARTICLES. Ashutosh Chilkoti, Duke University, Department of Biomedical Engineering.

I will describe the use of nanoparticles in the fabrication of biosensors and nanoscale biomaterials. In the first application, we have explored the use of gold colloids in suspension as a colorimetric reporter of the interfacial phase transition of environmentally responsive biopolymers. We observed that gold nanoparticles, onto which an ELP is immobilized, exhibit a large red-shift in their absorbance spectrum due to aggregation of the colloids due to the hydrophilic-to-hydrophobic phase transition of the immobilized ELP. This method

provides a simple and convenient colorimetric method to study the influence of the solution environment, interfacial properties and grafting method on the transition properties of environmentally responsive polymers at the solid-water interface. We have also immobilized gold nanoparticles onto glass slides, functionalized these surface with biological ligands, and shown that these colloid-decorated surfaces enable ligand-binding to be detected by the shift in the absorbance spectrum of individual colloids. This assay is analogous to conventional SPR with the added advantage of being performed in widely available, low-cost UV-visible spectrophotometers. Finally, we have developed a simple bottom-up nanofabrication method, ultraflat nanosphere lithography (UNSL), to create periodic nanopatterned surfaces of well-defined size and minimal topography comprising of two different materials that display orthogonal self-assembly chemistry. These ultraflat nanocomposites are useful for applications that range from surface-enhanced spectroscopy to the bottom-up fabrication of nanostructured biofunctionalized surfaces using chemical and biological self-assembly.

2:30 PM **Y6.3**

STABLE ADSORPTION OF LIPID VESICLES ON MODIFIED GOLD SURFACES. Stavroula Sofou, James L. Thomas, Columbia University, Dept of Chemical Engineering, New York, NY.

The use of vesicles as amplifiers in biosensors is receiving increasing attention. Because vesicles may entrap thousands of reporter molecules, strong signal amplification can be obtained if a small number of analytes can simply release the entrapped reporters. Surface immobilization of vesicles with sensitivities for different analytes could then provide for simultaneous amplified detection of a number of analytes on a single chip. To achieve this goal, vesicles must first be stably adsorbed to a surface, without rupture. We have varied vesicle composition and charge (phosphatidyl choline, phosphatidyl choline-phosphatidic acid at 4.6 molar ratio) and solution ionic strength, to study the adsorption of fluorescent vesicles to glass, gold, and gold modified with chemisorbed acetylcysteine. Surfaces were characterized with angle-resolved X-ray photoelectron spectroscopy (ARXPS), and vesicle integrity and behavior was studied using entrapped and/or lipophilic fluorescent markers. Diffusion coefficients (by photobleaching recovery) and vesicle fusion (by energy transfer) were monitored using confocal fluorescence microscopy. Finally, as a "proof of principle", release of a self-quenching entrapped reporter dye (calcein) by the detergent Triton X-100 was followed in real time.

2:45 PM **Y6.4**

ORDERING AND ANCHORING OF LARGE ORGANIC MOLECULES ON METAL SURFACES. Federico Rosei, Michael Schunack, Erik Laegsgaard, Ivan Stensgaard, Flemming Besenbacher, Univ of Aarhus, Institute of Physics and Astronomy, Aarhus, DENMARK.

Largish molecules have attracted great interest recently both from a fundamental point of view and for the possibility of applications in nanoelectronics, since they are the basic elements in the field of molecular electronics. Their adsorption behavior is thus of high interest. In the present study, we investigate the adsorption of "Lander" molecules $C_{90}H_{98}$ on the Cu(110) surface by Scanning Tunneling Microscopy (STM). The Lander molecule has a central polyaromatic molecular "wire" (conducting backbone), and four "spacer legs" (3,5-di-tert-butylphenyl substituents) for "isolation" from the substrate. We have nanostructured the Cu(110) substrate by exposing it to oxygen at elevated temperatures: the surface is thus patterned with alternating bare Cu regions and (2x1) reconstructed Cu-O rows, aligned parallel to the [001] direction. Upon deposition of the Lander molecules, we find that they avoid the top of the Cu-O rows, adsorbing exclusively on the bare Cu regions, and attaching to the edge of the Cu-O rows. This type of assembly opens new possibilities for ordering organic molecules on surfaces in a controlled manner: by changing the molecular coverage and oxygen exposure it is possible to obtain different types of ordered rows. Nano-manipulation experiments with the STM at low temperatures (100 - 200 K) performed on isolated molecules adsorbed on step edges revealed an underlying restructuring of the Cu steps: when removed from the step, a "tooth-like" structure appears; in this case, the Lander was deposited at Room Temperature. The structure's width is two atomic rows, corresponding to the distance between the spacer legs within the molecule. Repeating the same manipulation experiments on molecules adsorbed at low temperatures (150 K), no restructuring of the Cu step edges is found. The process is therefore thermally activated: the molecule induces the restructuring only when the mobility of the adatoms at the step edge is high enough.

3:30 PM ***Y6.5**

TOWARDS THE USE OF BIOLOGICALLY INSPIRED TECHNIQUES TO ASSEMBLE ELECTRONIC DEVICES. H. McNally^a, M. Pingle^b, S.W. Lee^a, D. Guo^a, D. Bergstrom^b, R. Bashir^{a,c}. ^aSchool of Electrical and Computer Engineering,

^bDepartment of Medicinal Chemistry, ^cDepartment of Biomedical Engineering Purdue University, W. Lafayette, IN.

Nature assembles nano-scale components using molecular recognition. In the case of DNA, hydrogen bonding is the driving force behind the matching of complementary pairs of single-stranded (SS) DNA to hybridize into a double strand of helical DNA. For the case of antibodies/antigens and ligands/receptors, binding takes place by a combination of electrostatic forces, chemical bonding, and shape mediated effects. In this project, we are investigating the assembly of micron sized and smaller particles using biologically inspired assembly. Following the case of DNA, a single strand sequence can be attached to the device surfaces, which is complementary to a single strand sequence previously attached to a patterned surface. Using the natural hybridization of DNA, the devices are expected to assemble in solution as designed onto the substrate surface. Long-range electrostatic forces may be used to bring the devices within range to allow for the hybridization to assemble the devices. We have also used a less complex molecule to add negative charges to the particles allowing them to be guided into place using electric fields. Attachment of these molecules to surfaces is a critical step in the assembly process. Various factors affecting the attachment are being investigated and will be reported. These include sample preparation, multiple point surface attachment, and conditions for attachment. The device size, weight, and shape factors are being investigated using multiple materials, including the silicon devices previously reported. When successful, this approach can be used to assemble micro and nano-scale electronic circuitry including heterogeneous integration of materials.

4:00 PM **Y6.6**

NANOFABRICATION AND CHARACTERIZATION WITH THE ULTRAHIGH VACUUM SCANNING TUNNELING MICROSCOPE ON THE Si(100) SURFACE. Lequn Liu, Jixin Yu, and J.W. Lyding, Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL.

Recently, ultra high vacuum (UHV) scanning tunneling microscopy (STM) is used to selectively desorb hydrogen from the Si(100)2x1:H surface so as to make atomic scale patterns and selectively adsorb molecules. In order to understand well the chemical interactions between the dangling bonds and molecules, the electrical properties of single dangling bonds were investigated on the Si(100)2x1:H surface by UHV-STM. On the N type Si(100)2x1:H surface, feedback-control-lithography (FCL) created single dangling bonds and some of natural dangling bonds have a fixed negative charge, while some of natural single dangling bonds are neutral. On the other hand, both FCL created and natural single dangling bonds are neutral on P type Si(100)2x1:H surface. Current image tunneling spectroscopy (CITS) measurements demonstrate different electrical properties on them. Specially, the STM images of the single dangling bonds with a fixed negative charge display dramatic voltage dependence with Friedel oscillations around these dangling bonds in the empty state images. Isolated Cobalt phthalocyanine (CoPc) molecules were selectively adsorbed on both the natural dangling bonds of the Si(100)2x1 surface and FCL created single dangling bonds on the Si(100)2x1:H surface. On the Si(100)2x1 surface, three major adsorption configurations were observed consisting of a four-fold molecular image characteristic of CoPc but possessing different central structural features. However, images obtained on the Si(100)2x1:H surface correspond to molecular rotation of CoPc parallel to the surface. STM, STS, CITS and molecular modeling are used to investigate the different interactions between CoPc and these two Si substrates, as well as their effects upon the electronic charge distribution and the geometric configurations of the adsorbed CoPc molecules. This study may be useful for making molecular-scale RAM.

4:15 PM **Y6.7**

PREFERENTIAL ADHESION OF GOLD NANOPARTICLES USING LITHOGRAPHICALLY PATTERNED SUBSTRATES. Johan Pihl, Mohammad S. Kabir, S.H. Magnus Persson, Chalmers Univ of Technology, Dept of Microelectronics and Nanoscience, Gothenburg, SWEDEN; Mathias Brust, Liverpool Univ, Dept of Chemistry, Liverpool, UNITED KINGDOM.

In the area of molecular electronics, the electrical properties of nanoparticles and molecules connecting them is a big issue, but there exists considerable problems in making well defined electrical measurements on them, and there are often difficulties in knowing over what particles the measurements are really taking place. By using silicon substrates patterned with silanes or silazanes having different endgroups by chemical vapour deposition and electron beam lithography, small arrays of gold nanoparticles have been assembled between narrowly spaced electrodes. This enabled the possibility to make well defined electrical measurements of the nanoparticles, and also on conjugated disulphides and diselenols with interesting electrical properties

4:30 PM **Y6.8**

DIRECT PATTERNING OF SURFACES WITH COLLOIDAL PARTICLES USING OPTICAL TWEEZERS. Dirk L.J. Vossen, Jacob P. Hoogenboom, Karin Overgaag and Alfons van Blaaderen, F.O.M. Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS; Physics and Chemistry of Condensed Matter, Debye Institute, Utrecht University, THE NETHERLANDS.

We describe a method for patterning substrates with colloidal particles in any designed pattern. By using optical tweezers particles are brought from a reservoir to a surface that carries a surface charge opposite to that of the particles. We show that using this technique large, two-dimensional patterns can be created, where the pattern can be manipulated on a single particle level. Furthermore, we show that this method works for a large variety of functionalized (core-shell) colloidal particles. Particles that can be manipulated by means of optical tweezers include particles that are interesting for photonic applications like high-refractive index (ZnS) core silica shell particles, metallic (Ag) core - silica shell particles, fluorescently labelled particles and small (several nanometers large) gold particles. Particle sizes range from several nanometers to over a micrometer. We show how these two-dimensional patterns can be dried for further processing and how these patterns can be used in subsequent three-dimensional epitaxial crystal growth. The method works relatively fast, is cheap, can be fully automated and can in principle be used to build three-dimensional structures as well.

4:45 PM **Y6.9**

PATTERNING OF QUANTUM DOTS USING NANOPOROUS ALUMINA. N. Presser, M.B. Tueling, D.M. Speckman, S.D. LaLumondiere, and T.L. Jennings, The Aerospace Corporation, Los Angeles, CA.

Simple, high throughput, low cost methods for the deposition of patterned nanocrystal arrays on substrate surfaces is necessary for the development of the next generation of electronics based on molecular-scale devices. As the need for higher storage densities, faster computing ability, and reduced power requirements increases, device dimensions in integrated circuits must continue to shrink. Miniaturization of magnetic- and silicon-based devices is becoming increasingly difficult due to limitations of optical photolithography and due to the problems associated with high device densities, such as "cross-talk" and inadequate heat dissipation. Theoretically, ordered arrays of quantum dots can be used to build complex computing systems, which, unlike traditional electronic devices and interconnects, do not rely on current flow. The ability to deposit and/or grow semiconductor quantum dots in appropriate nanopatterned arrays is currently the single greatest technological hurdle to be overcome before these technologies can seriously be considered. We report here a simple, rapid, and inexpensive method for producing nanoarrays of CdSe/ZnS semiconductor quantum dots, using nanoporous alumina. Highly ordered arrays of nanopores, approximately 20-200 nm in diameter, can be produced in very thin sheets of aluminum metal using a carefully controlled anodization process. We have successfully trapped CdSe/ZnS nanocrystals (approximately 30 nm in diameter) within these highly ordered nanoporous structures, and have characterized the optical properties of the trapped nanocrystals. We will describe the details of this process and discuss our spectroscopic results.

SESSION Y7: POSTER SESSION
MATERIALS AND NANOFABRICATION
TECHNIQUES FOR ELECTRONIC AND
BIOLOGICAL APPLICATIONS

Chair: Lhadi Merhari
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

Y7.1

EFFECTS OF MASK MATERIALS ON NEAR FIELD OPTICAL NANOLITHOGRAPHY. Sharee McNab, Richard Blaikie, University of Canterbury, Dept Electrical and Electronic Engineering, Christchurch, NEW ZEALAND.

Sub-diffraction-limited resolution has been reported for optical lithography in the near field of an amplitude mask [1] and simulations predict resolution down to 10nm [2]. In addition, an evanescent interferometric lithography (EIL) technique has been proposed for patterning periodic nanostructures [3]. The studies to date have employed standard metallic masking materials, chrome or nichrome. We have performed a simulation study on the effects of different masking materials on these techniques. Chrome, gold, tungsten and silicon have been chosen as common microelectronic materials that can be patterned down to the nanometre scale. For near field amplitude masks it is found that chrome is an excellent material at

blue/UV wavelengths, due to its small skin depth. Gold is too transmissive to be considered. Tungsten has a small skin depth like chrome, although its dielectric behaviour at blue/UV wavelengths leads to image reversal phenomena that may be undesirable. Image reversal is even more pronounced for silicon masks, but significant field enhancement effects are observed that may be beneficial for reducing exposure times. For EIL the mask material issues are more complicated, as this technique relies on surface-plasmon-induced resonant enhancement of the evanescent fields beneath a grating. For metallic materials, chrome is again superior to gold, and significant intensity enhancements are predicted beyond the grating cutoff. For silicon the resonant enhancements can be very large and narrow band, which may be of great advantage. For example, intensity enhancements of more than 20 times are predicted for 270nm period silicon gratings illuminated at a wavelength 10 percent higher than cutoff. These issues will be discussed in detail.

1. Alkai, et al., Appl. Phys. Lett. 75, 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).

Y7.2

PYROELECTRIC EMISSION FOR LITHOGRAPHY. Changwook Moon, Wonbong Choi, Eunju Bae, Dongwook Kim, In Kyeong Yoo, Samsung Adv Inst of Tech, Suwon, Kyongki, KOREA.

1:1 electron projection lithography with wide projected area was studied by patterning images and measuring emission current utilizing pyroelectric electron emission from ferroelectric material. It was observed that the pyroelectric emission is suitable for a 1:1 electron projection lithography application. Focused images of 1:1 electron projection were patterned on the e-beam resist by controlling magnet-electric system in vacuum. Theoretically, pyroelectric electron emission has the potential to give a perfect resolution in 1:1 electron projection lithography. The 1:1 PEL (pyroelectric emission lithography) method has several advantages over conventional lithography technologies such as pyroelectric emitter will be used semi-permanent life cycle due to its recycle after heating above T_c and 1:1 PEL can increase throughput due to its capability of wide area electron projection. We have demonstrated 1:1 electron projection lithography on electron resist by heating a polycrystalline BaTiO₃ emitter with a grid pattern. It was observed that a poling process was not necessary for pyroelectric emission when high PS materials are used, i.e., polycrystalline BaTiO₃. Heating the emitter above its T_C during the lithography process eliminated the degradation of the pyroelectric emission effect. An approximated relationship among emitter-collector distance, applied DC voltage, and magnetic fields was studied systematically. This paper will describe new design concepts for 1:1 PEL and provide controlling factors for obtain fine patterning.

Y7.3

CHARACTERIZATION OF La/B₄C MULTILAYER MIRRORS FOR X-RAYS BELOW 190 eV. Stefan Hollensteiner, Christel Dieker, Wolfgang Jaeger, University of Kiel, Center for Microanalysis, Faculty of Engineering, Kiel, GERMANY; Carsten Michaelsen, Joerg Wiesmann, Ruediger Bormann, Institute of Materials Research, GKSS Research Center, Geesthacht, GERMANY; C. Nowak, HASYLAB, DESY, Hamburg, GERMANY.

Metastable multilayer systems based on metal-nonmetal combinations with layer thicknesses in the nanometer range are of increasing interest for advanced X-ray optical applications. We have fabricated La/B₄C multilayer films by magnetron sputtering for the use as X-ray mirrors at energies below 190 eV, particularly for the detection of boron K X-rays at 183 eV, and compared them to Mo/B₄C multilayers that are currently the best-performing multilayers for this energy range. Transmission electron microscopy, low-angle X-ray diffraction and synchrotron soft X-ray reflectometry at energies between 50 eV and 525 eV were used to study the structure and interfaces of the multilayers, their thermal stability up to 800C, and their performance as X-ray optical component. In general the microscopic structure of the layer systems after deposition is characterized by an excellent structural periodicity and interface quality. Depending on the fabrication process, the interfaces between the individual amorphous layers may show a different roughness. Only small fractions of oxygen and argon are present in the multilayers as could be shown by energy-dispersive X-ray microanalysis and by X-ray photoelectron spectroscopy. Both the peak reflectivity and the spectral purity are found to be significantly improved indicating that La/B₄C multilayers have a high potential to replace state-of-the-art Mo/B₄C multilayers in many X-ray optical applications below 190 eV. Both multilayer systems were also compared by laboratory XRF measurements of the boron K emission using samples of B₄C and of BPSG (borophosphosilicate glass). For the La-based multilayer systems the improvements of the peak intensity and the lower limit of detection amount to about 64% and 29%, respectively.

Y7.4

NOVEL FLUOROCARBINOLS FOR 157 NM PHOTOLITHOGRAPHY. Hilmar Koerner, Young C. Bae, Katsuji Douki, Dirk Schmaljohann, Patrick E. Spencer, Vaishali R. Vohra, Xiang-Qian Liu, and Christopher K. Ober; Cornell University, Dept of Materials Science and Engineering, Ithaca, NY.

157 nm photolithography is the foremost candidate in next generation resist technology to date. This requires a reconsideration of the fundamental understanding of how each of the components of the resist interact with one another and how those changes affect resist performance. There are primarily three approaches that our group is embarking on to overcome the obstacles of 157 nm photolithography. One of them includes the use of block copolymers. This study was initialized by our findings in excellent etch resistance of hexafluoroacetone modified poly(isoprene), that has been cyclized and protected to provide good transparency and solubility switch. Fluorinated poly(vinyl acetate) polymers on the other hand can be protected by more desirable protecting groups, such as dihydropyran, to yield relatively transparent tetrahydropyranyl (THP) at 157 nm. However, the most promising strategy is similar to the one that has been applied to 248 nm photoresists. Our system is based on monomers carrying the hexafluoroisopropyl alcohol (HFIPA) group. This concept has been first introduced in the design of polystyrene-based resists for 248 nm. Unfortunately, protecting groups used in those cases are too absorbent at 157 nm. It has been shown that alkoxyethers are the most suitable groups for protection of HFIPA groups. In order to achieve a material with good chemical amplification, copolymers of our novel superfluorinated monomer system were synthesized with THPMA as a comonomer. Even with relatively high carbonyl group contents these copolymers show an absorbance of only 2/micron at 157 nm and feature sizes down to 80 nm in excellent resolution. Further improvement of etch resistance could be achieved by using HFIPA modified styrenic monomers. We will show that our new resist platforms are excellent candidates to push photolithography closer to the 70 nm node.

Y7.5

3-D MICROFABRICATION IN A CHEMICALLY AMPLIFIED POSITIVE RESIST. Tianyue Yu and Christopher K. Ober, Materials Science and Engineering, Cornell University, Ithaca, NY; Stephen M. Kuebler, Wenhui Zhou, Seth R. Marder and Joseph W. Perry, Department of Chemistry, The University of Arizona, Tucson, AZ.

Three-dimensional microfabrication has a wide range of possible applications for micromachining structures such as light-waveguides, microfluidic devices, MEMS and data storage. Two-photon lithography not only allows the fabrication of structures not feasible with conventional single-photon lithography but also exhibits greater spatial resolution than other three-dimensional fabrication techniques as currently practiced. In contrast to UV lithography, where the photoresist serves only as a pattern transfer layer, in 3-D lithography, the photopolymer can form the final structure or act as a template for pattern transfer. Thus the resin systems should not only be two-photon sensitive but also possess some necessary properties to meet the requirements of the applications listed above. From early work in two-photon three-dimensional fabrication, volume shrinkage and warping of solid images formed in these processes were identified as key areas where the method can be improved. Little research has been carried out to identify a more suitable system for three-dimensional microfabrication. We focus on developing a solid-state, chemically amplified positive-tone resist system which offers reduced shrinkage and greater patterning versatility by using a different solubility switch mechanism. Here, we will report the design and microfabrication of an optical grating structure with a series of channels buried below the surface and some key processing conditions will be discussed as well.

Y7.6

NOVEL MATERIALS FOR 157 NM AND EUV LITHOGRAPHY. Alyssandrea H. Hamad, Junyan Dai, Christopher K. Ober, Cornell University, Ithaca, NY; Francis M. Houlihan, Agere Systems, Murray Hill, NJ.

The design and synthesis of lithographic materials for 157 nm and extreme-ultraviolet (EUV) lithography has been a challenge. Polymers and small molecules traditionally used for lithography are highly absorbing at these wavelengths. Carbon double bonds and carbonyls are opaque at 157 nm in the absence of neighboring electron-withdrawing groups. Few elements can be used in an EUV photoresist due to absorbance requirements and resist chemists are restricted to the use of elements such as carbon, hydrogen, and silicon for these platforms. For example, oxygen, an element of crucial importance in earlier photoresist generations, absorbs highly at 13 nm and therefore, its use is restricted in EUV lithography. Here, we will report on the design, synthesis, and properties of new silicon-containing block

copolymers and random copolymers for EUV lithography. In addition, we wish to report on fluorine and silicon-containing dissolution inhibitors for 157 nm lithography. Initial studies on our EUV resists as well as dissolution rate studies on our 157 nm dissolution inhibitors will be discussed.

Y7.7

SUPERCritical CO₂ DEVELOPMENT FOR ADVANCED PATTERNING OF RESIST AND DIELECTRIC MATERIALS.

Victor Q. Pham, Gina L. Weibel, Alyssandrea H. Hamad, Christopher K. Ober, Cornell University, Dept of Materials Science and Engineering, Ithaca, NY; Hilton Pryce Lewis, Karen K. Gleason, MIT, Dept of Chemical Engineering, Cambridge, MA.

As sizes of patterned features in polymer resists become smaller (and aspect ratios become larger), the concept of a post-development supercritical drying step has been suggested to prevent pattern collapse due to surface tension. A model photoresist system, tetrahydropyranyl methacrylate-co-1H,1H-perfluorooctyl methacrylate (THPMA-F7MA), was synthesized in both block and random copolymers and shown to be highly compatible with 193 nm and E-beam exposure technologies. Well-defined 100 nm features have been achieved when the block copolymer was developed in supercritical CO₂, eliminating the need for organic developers or a drying step. With increasing understanding of polymer-CO₂ interactions and subsequent process optimization, higher resolution features are expected to demonstrate technological advantages over wet development. An interferometric dissolution rate monitor (DRM) was built to probe the kinetics of polymer dissolution in SCF CO₂. Our high-pressure system has yielded interesting and reasonable results including equilibration behavior of CO₂ liquid converted rapidly to supercritical in the processing chamber. In addition to resists, a patternable dielectric material was CVD deposited from hexafluoropropylene oxide (HFPO) precursor, patterned using EB Lithography, and developed in similar CO₂ conditions. The success of a patternable dielectric will possibly eliminate the need of a sacrificial resist and several processing steps in IC manufacturing. Insights to the CO₂ equilibration process and an understanding of CO₂ interactions with fluorinated materials are instrumental to our current efforts toward the adoption of dry lithography.

Y7.8

DESIGNING PHOTORESIST SYSTEMS FOR MICRO-

LITHOGRAPHY IN CARBON DIOXIDE. Devin Flowers, Univ of North Carolina-CH, Dept of Chemistry, Chapel Hill, NC; Chris McAdams, Micell Integrated Systems, Raleigh, NC; Erik Hoggan, Ruben Carbonell, North Carolina State Univ, Dept of Chemical Engineering, Raleigh, NC; Joseph M. DeSimone, Univ of North Carolina-CH, Dept of Chemistry, Chapel Hill, NC, North Carolina State Univ, Dept of Chemical Engineering, Raleigh, NC, Micell Integrated Systems, Raleigh, NC.

Currently, the microlithography industry creates large amounts of organic and aqueous wastes in the production of semiconductors. Using carbon dioxide can possibly eliminate the majority of these waste solvents as well as eliminate the image collapse problems shown with aqueous base development. We will discuss the use of carbon dioxide to replace the most solvent intensive steps of the microlithography process, spin coating and developing. However, before CO₂ can replace conventional solvents, photoresist systems must be designed and synthesized to be compatible with CO₂. These photoresist systems must be soluble in liquid CO₂ to insure that thin-uniform coatings can be produced by spin coating while maintaining characteristics of conventional resist systems such as low absorbance, high sensitivity, solubility contrast, good resolution, and etch resistance. In this paper we will present our efforts to create these photoresist systems for 193nm and 157nm lithography by using fluorinated components of conventional resist systems thus rendering them soluble in CO₂. Fluorine-based acrylates have been used as a resin for the 193nm resist system. However, the 157nm resins we are designing are fluorine-based norbornyl copolymers with tetrafluoroethylene, maleic anhydride, or 2-trifluoromethyl acrylates. Currently, the key issues are making these systems both soluble in liquid CO₂ and while maintaining a Tg around 120C. We have also designed a liquid CO₂ soluble photoacid generator, 2-perfluorohexyl-6-nitrobenzyl tosylate, which has been shown to be effective in reducing the cleaving temperature of the t-butyl leaving groups.

Y7.9

NON-EQUILIBRIUM LAYER-BY-LAYER GROWTH OF BINARY COLLOIDAL CRYSTALS. Christina G. Christova^a, Krassimir P.

Velikov^a, Roel Dullens^a and Alfons van Blaaderen^{a,b}. ^aPhysics and Chemistry of Condensed Matter, Debye Institute, Utrecht University, Utrecht, THE NETHERLANDS. ^bFOM Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

A mixture of submicron colloidal particles of two sizes can self-organize into binary crystals, which depending on the size ratio and concentration can have different crystal symmetries. Colloidal crystals with lattice constants comparable to the wavelength of visible light are important for applications and processes as diverse as photonic crystals, chemical sensors, lithography, surface enhanced Raman scattering, and the creation of mesoporous materials. However, binary colloidal crystals have not been used for these applications mainly due to lack of control in growing them. Here we present a method to grow binary colloidal crystals in a controlled way, through a simple, layer-by-layer drying process. In this non-equilibrium process hydrodynamic and surface tension effects play a role next to epitaxial effects and the decrease in the chemical potential that drives bulk crystallization. We were able to generate well-ordered and large ($200 \mu\text{m}^2$) single binary colloidal crystals with a stoichiometry of large (L) and small (S) particles of LS_2 (atomic analog AlB_2) and unexpectedly, LS . In addition, we observed the formation of an LS_3 superstructure, which is not identified yet to any known molecular compound or alloy. Both the binary crystals with stoichiometry LS_2 and LS_3 can be grown without stacking faults in this process. Finally, by using spheres with different composition, one component can be removed. As an example, we demonstrate the synthesis of a hexagonal non-closely packed colloidal crystal. As the method presented is quite general and can be extended to include more sizes, it will lead to a significant increase in the possible symmetries and compositions achievable for colloidal crystals.

Y7.10

EFFECT OF Al CONCENTRATION ON GROWTH OF ANTIPHASE DOMAINS IN Ti_{13}Al . Yuichiro Koizumi, Hideaki Katsumura, Yoritoshi Minamino, Nobuhiro Tsuji, Osaka Univ, Dept of Adaptive Machine Systems, Osaka, JAPAN.

In many intermetallic compounds with ordered structure, antiphase boundaries (APBs) are formed during the ordering process. Since the APBs can trap dislocations and assist in the self-assembly process of dislocations, it is possible to make regular arrangement of dislocations in nanoscale by controlling the morphology of APBs, i.e., size and shape of antiphase domains (APDs) which are regions divided by APBs. Such regular arrangements of dislocations are expected to give unique mechanical properties, for example, 'completely reversible plasticity'. Ti_{13}Al intermetallic compound is one of the most useful material to make such mechanical properties real. However, no attempts have been done to control the morphology of APBs in Ti_{13}Al . In this study, Ti_{13}Al crystals with stoichiometric (Ti-25at.%Al) and Al-rich (Ti-33at.%Al) compositions were annealed at various temperatures (973~1173K) subsequently to disordering treatment. And the effects of Al-concentration on change in the morphology of APDs were investigated. Remarkable effects of Al concentration were found. Firstly, growth rate of APDs in the Al-rich crystals was several times as high as that in the stoichiometric crystals. Secondly, time dependence of APD size varied during annealing only in the Al-rich crystal. While the APD size was always proportional to the square root of annealing time ($t^{1/2}$) in the stoichiometric crystals, the time exponent became smaller than 1/2 at later stage in the Al-rich crystal, indicating the existence of dragging force acting to the motion of APBs. Additionally, APBs aligned along (0001) and $1\bar{1}00$ planes were observed only in the Al-rich crystal annealed at the lowest temperature. The reasons for the difference between changes in the morphology of APBs in these compounds are discussed focusing on the effects of Al concentration on driving force and mobility of APBs.

Y7.11

AFM STUDIES OF FRACTURE SURFACES OF COMPOSITION B ENERGETIC MATERIALS. Y.D. Lanzerotti, U.S. Army TACOM-ARDEC, Picatinny Arsenal, NJ.

In this paper the characteristics of TNT crystals in Composition B (59% cyclotrimethylene (RDS), 40% TNT and 1% wax) at the fracture surface using AFM are presented. The size of the TNT crystals has been determined by analyzing the surface structure after mechanical failure of the Composition B. The sample of melt-cast Composition B used for the AFM studies fractured at 46 Kg in an ultracentrifuge. AFM examination of the topography of the fracture surface of the Composition B reveals fracture across columnar grains of the TNT. The width of the columnar TNT grains range from $\sim 1 \mu\text{m}$ to $\sim 2 \mu\text{m}$. The height of the columnar TNT grains range in size from $\sim 50 \text{ nm}$ to $\sim 300 \text{ nm}$. We have introduced AFM techniques to characterize the fracture surface topography of Composition B obtained at high acceleration. Using AFM we have measured the size of the columnar TNT grains of Composition B and have determined that the fracture of the Composition B occurs within the TNT.

Y7.12

OPTIMUM CONDITIONS FOR SELF-ORDERED GROWTH OF POROUS ALUMINA. Kornelius Nielsch, Ralf B. Wehrspohn, Jinsub

Choi, Herbert Hofmeister and Ulrich Gösele, Max-Planck-Institute of Microstructure Physics, Halle, GERMANY.

Hexagonally-arranged porous alumina is an emerging material used as non-lithographic imprint stamp or template for the fabrication of well-defined nanowire arrays. The conditions for the self-organized formation of highly ordered hexagonal pore channel arrays in anodic alumina were investigated with different acidic electrolytes. Five different growth regions, where a self-assembly of the pore channels occurs, have been identified at an interpore distance of 50 and 65 nm for sulphuric acid, 100 nm for oxalic acid and 420 and 500 nm for phosphoric acid. In analogy to a 2D-polycrystalline structure, the pore channels are hexagonally arranged in domains. The domain size increases non-linearly during the anodization and can be extended over more than ten lattice periods. The mechanical stress resulting from the volume expansion during oxide formation is proposed to cause repulsive forces between the neighboring pores which promote the self-assembly. We will show, that the conditions for the self-organized growth are correlated to the voltage and the type of electrolyte. Both parameters determine the volume expansion of the aluminum during oxidation and the current efficiency for oxide formation. Moreover, the internal oxide structure was investigated by transmission electron microscopy. Similar as in the case of biological cells, the pore channel in the center of a single pore cell is surrounded by a thick anion contaminated oxide layer and the outer cell wall consist of a thin relative pure oxide wall. In contrast to earlier publications on unarranged alumina pore structures, the thickness ratio of the two oxide regions and the template porosity are nearly constant and independent of the applied electrolyte for all five highly ordered pore structures. A strategy for making accessible new regimes of pore growth with interpore distances between 100 and 400 nm is given.

Y7.13

FORMATION OF ALUMINUM NANODOT ARRAY BY THE COMBINATION OF NANO-INDENTATION AND ANODIC OXIDATION. Shoso Shingubara, Yasuhiko Murakami, Kazunori Morimoto, Hiroyuki Sakaue, Takayuki Takahagi, Hiroshima University, Graduate School of ADSM, Higashi-Hiroshima, JAPAN.

A method to form a nanometer size two-dimensional Al dot array was developed by the combination of nano-indentation and Al anodic oxidation. Porous alumina films which were formed by Al anodic oxidation has been intensively studied to use them as molds to form nanowires or dots by depositing various metals or semiconductors in them [1]. There are limited self-organization conditions to form the ordered array of nanoholes by the use of oxalic acid, sulfuric acid, or phosphoric acid. We found the self-organized formation of Al hexagonal dot array on Si by selective wet chemical etching of porous alumina film using the mixture of phosphoric acid and chromic acid [2]. However, control of its size and geometry are limited by the self-organization condition. We introduced AFM nano-indentation technique to initiate formation of nanoholes at the beginning of anodic oxidation. Al film with thickness of 100 nm was sputter-deposited on Si substrate covered by SiO_2 . Then nano-indentation was carried out on a flat Al surface to form two dimensional periodic surface roughness with 200 to 70 nm nearest neighbor distance. Anodic oxidation with oxalic acid was carried out, and alumina film was selectively etched away. Al dot square lattice arrays were successfully formed after selective wet chemical etching of porous alumina film. The most ordered Al dots were obtained at the 90 nm nearest neighbor distance, which seemed to come from anodic voltage of 40V. Further investigation to reduce the size by a suitable choice of indentation as well as anodic oxidation conditions are in progress.

[1] S. Shingubara, O. Okino, Y. Sayama, H. Sakaue, and T. Takahagi Jpn.J.Appl.Phys.vol.36 No.12 (1997) pp.7791-7795.

[2] Y. Murakami, S. Shingubara, H. Sakaue, and T. Takahagi, Proc. of Microprocesses and Nanotechnology 2000, (2000) pp. 178-179.

Y7.14

ORDERING EFFECT OF LITHIUM IONS IN A SELF-ASSEMBLED HYBRID SYSTEM. Jaime Retuert, Sandra Fuentes, Guillermo Gonzalez, Juan Fernandez, Univ de Chile, Santiago, CHILE.

By blending 3-aminopropyl-siloxane oligomers (pAPS) with chitosan (CHI) self-assembled hybrid films have been obtained. Films obtained from a CHI/pAPS with 0.6:1 molar ratio were flexible and transparent, indicating compatibility of the components at molecular level. Moreover, for this composition a intermolecular complex is formed. Video-Enhanced Differential Interference Contrast Microscopy (VEC-DIC) showed that films consisted of outer and inner layers. Globules that fit in pits of the inner layer formed the outer layer. The latter constituted an egg-box-like structure. Considerable amount of LiClO_4 can be homogeneously incorporated in the hybrid composite, but this transform the film globular pattern into a smoother, nearly flat pattern. Such changes in the morphology and DRX diffractograms could be interpreted as a new organization of the complex structure

due to the participation of functional groups in coordinating Li ions. In this work we present new results obtained by studying the addition of LiClO₄ when this salt is included in the hybrid material with amounts corresponding to the limit of maximal homogeneous incorporation. This corresponds to the composition CHI/pAPS/LiClO₄ = 0.6/1/0.8M. For this composition, VEC-DIC Microscopy of the first three layers of the films showed that each layer have oriented patterns with angles of exactly 60 degrees between the planes. On the other hand, DRX showed that some sharp new peaks appear with the incorporation of the lithium salt. The same signals appears by incorporating lithium chloride or triflate. However, no peak attributable to the corresponding lithium salt was observed in films with homogeneous incorporation of the salt. These results in combination with FTIR analysis of the products indicates that lithium ions behaves as strong structure directing agent and allowed us to propose an interaction scheme comprising the components of this hybrid system.

Acknowledgments: Projects Fondecyt 1010525, 1010924 and 297004.

Y7.15

POLYMERIC ALL SOLID-STATE NANOSCALE BATTERY.

Steven E. Bullock, and Peter Kofinas, University of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

The goal of the proposed research is to synthesize A/B/C triblock copolymer - metal nanocomposites and evaluate their electrical properties for the fabrication of all-solid state nanoscale batteries. The ease of processing a polymer electrolyte would allow the production of a thin film battery that could be wound into coils or processed as sheets. The A/B/C triblock copolymer battery would exhibit a lamellar microphase separation, with anode, polymeric electrolyte and cathode as the A, B and C blocks, respectively. The A block (organometallic cobalt) forms the anode material and the B block (polyethylene oxide) is the electrolyte. The C block (functionalized norbornene) is the cathode material and utilizes a hydride reduction. Casting of the synthesized polymer from a solvent results in a self-assembled lamellar A/B/C nanostructure, which is equivalent to many battery cells in series. Microstructure and electrical properties characterization tools are employed to evaluate the battery system's performance.

Y7.16

ELECTRIC FIELD ASSISTED DEPOSITION AND DETERMINATION OF THE ELECTROSTATIC PROPERTIES OF CdSe NANOPARTICLES. Mohammad A. Islam and Irving P. Herman, Columbia University, Materials Research Science and Engineering Center and Columbia Radiation Laboratory, New York, NY.

CdSe nanoparticles of 3.2 nm diameter capped by tri-n-octylphosphine oxide were deposited on Au electrodes by the assistance of strong electric field. A pair of Au-on-Si electrodes separated by 1.4 mm was submerged in the nanoparticles dissolved in 90% hexane and 10% octane and voltages of the order of 300 V were applied in a dark room. When the electrodes were submerged in only the solvent, current was measured to be ~ 1 - 2 nanoamperes. When the nanoparticles were added to the solvent, current immediately jumped up to the 50 - 100 nanoamperes range, depending on the nanoparticle concentration and the size of the electrodes. The current was found to increase linearly with the applied voltage, electrode area and nanoparticle concentration. The nanoparticles were deposited on the positive electrode only, showing that they were negatively charged in these experiments. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to determine the morphology of the deposit. The nanoparticles make micron sized islands on the electrode. The islands are few hundred nanometers in height and have sharp edges indicating that the nanoparticle assembly may be crystalline. The total number of particles deposited in a given time and the deposition rate are determined from SEM and AFM. This work was supported by the MRSEC program of the National Science Foundation, Contract No. DMR-9809687.

Y7.17

EXCIMER LASER MICROMACHINING OF WIDE BAND GAP SEMICONDUCTOR WAVEGUIDE FOR NANO-SCALE CAGED MOLECULE DRUG DELIVERY. Mona R. Safadi, Claudine A. Jaboro, Alexander L. Lagman, Gregory W. Auner, Department of Electrical and Computer Engineering/Biomedical Engineering, Wayne State University, Detroit, MI; Gary Abrams, Raymond Iezzi, Pat McAllister, School of Medicine, Kresge Eye Institute, Department on Neurosurgery, Ligon Center for Vision, Wayne State University, Detroit, MI; Ratna Naik, Department of Physics, Wayne State University, Detroit, MI; Vaman M. Naik, Department of Natural Sciences, University of Michigan-Dearborn, MI.

The fabrication of a broad spectrum AlN thin film wave guide used in a nano-sized caged neurotransmitter based microfluidic drug delivery

chip is reported. The wave guide will be used in an artificial retina system along with other applications where spatially controlled amounts of nano-scale molecules of neurotransmitter are needed. KrF Excimer laser micromachining technology is employed in the development of the wide band gap waveguide. Highly textured AlN thin films are grown on C-plane sapphire by plasma source molecular beam epitaxy (PSMBE). A 248 nanometer Excimer laser beam is projected through a patterned stainless steel mask and through an objective lens down to 0.1 times of the actual pattern of the mask on to the AlN/sapphire substrate. The irradiation energy per pulse, frequency or repetition rate, and number or pulses were varied, while the beam profile, wavelength and pulse duration were held constant. Atomic force microscopy and scanning electron microscopy are used to characterize device structure. A calibrated photodiode was used to measure the intensity of ultraviolet light through the wave-guiding micro-channels. Wave-guide properties are characterized as a function of AlN film thickness and waveguide geometry. Results of a precise method in fabricating a prototype microfluidic waveguide system for nano-drug delivery will be presented.

Y7.18

MICRO- AND NANOFABRICATING LIPID PATTERNS USING A POLYMER-BASED WET LIFT-OFF. Reid N. Orth, Dept of Biomedical Engineering; Bojan Ilic, Harold G. Craighead, Dept of Applied and Engineering Physics, Ithaca, NY.

Lipid molecules were immobilized on the surface of silicon using a Parylene wet lift-off technique. Large unilamellar 1-palmitoyl 2-oleoyl phosphatidylcholine lipid vesicles were found to bind on the native oxide surfaces of silicon. Projection lithography and reactive ion etching were used to pattern a Parylene coated surface reliably to sub 4 μm features, which was subsequently coated with a lipid bilayer. The polymer is peeled away while submerged in deionized water from the substrate leaving the desired lipid pattern. The Parylene wet lift-off technique was compared to the lipid microcontact printing on silicon. Patterning was performed using several different lipid conjugated biomolecules (polyethylene glycol (PEG), biotin, fluorescence dyes, and DNA oligomers).

Y7.19

PATTERNED NANOPARTICLE ASSEMBLY AS NOVEL CHEMICAL AND BIOLOGICAL PLATFORMS. Mathew M. Maye, Jin Luo, Li Han, Chuan-Jian Zhong, Dept of Chemistry, State University of New York at Binghamton, Binghamton, NY.

The abilities to assemble nanoparticles with controlled size, shape and surface properties and subsequently to probe the nanostructures are crucial for exploring nanoscale biomimetic and biological functional properties. In this presentation, we will describe a novel approach to nanoparticle assembly at micro-patterned platform. Recent findings of scanning force microscopic investigation of biomimetic functional properties at such a platform of the nanoparticle assemblies will be discussed. Highly monodispersed nanocrystals produced by thermally-activated processing and functionalized molecular linkers are utilized to assemble nanoparticle thin film architectures. Such nanomaterials impart biomimetic ion-channeling properties at the nanostructure/liquid interface under pH-tuning. By probing nanoparticle assembly on patterned surfaces as a platform with micron-sized addresses, the microscopic results of both friction force and topography revealed intriguing morphological changes associated with the nanostructured biomimetic activity and antibody-antigen interactions. Both qualitative and quantitative data about the ionic and solvent fluxes in and out of the nanostructured membrane in solution are acquired, which allow us to gain insights into the detailed interfacial structures and processes. The results will be discussed for delineating the interfacial molecular interaction and the nanostructured biomimetic and biological functions.

Y7.20

MANIPULATION OF DNA VIA ATOMIC FORCE MICROSCOPY. J. Braun, D. Lagally, S.D. Gillmor, K. Moloni, S. Limbach, D. van der Weide, and M.G. Lagally, University of Wisconsin-Madison, Madison, WI.

Scanned probe microscopy techniques have shown themselves to be extremely versatile, extending beyond microscopy to include lithography and other novel applications in which a probe that is mechanically scanned with nanometer resolution is desired. Dip-pen lithography, using the AFM tip in a manner similar to a quill pen, shows promise as a novel method to write with alkanethiols as well as other organic solvents onto surfaces on the nanometer scale*. We focus on using AFM with a functionalized carbon nanotube tip to move DNA on surfaces, placing it at desirable locations to attempt to create an array with nanoscopic amounts of material. Nanotube AFM tips have the advantage of a high aspect ratio and can image a trench or a channel with greater precision than a traditional AFM tip. A nanotube dip-pen method can deposit solvent or other material in

such a 3D topology. We have chosen to work with DNA, as it is a useful biological molecule, although expansion to other molecules is foreseeable. In a humidity-controlled environment, a small droplet of condensed DNA solution is deposited on a mica surface. A functionalized nanotube affixed to an AFM tip is subsequently immersed in the solution, and the chemical attraction aids in the transfer of DNA and solvent to the nanotube. When the tip is coated with solvent, we can deposit solvent and DNA, like ink in a pen, in bundles of 50nm in diameter, at specific locations on the mica surface. We discuss the difficulties and the promise of this technique.

Supported by NSF.

*R.D. Piner, J. Zhu, F. Xu, S. Hong, C.A. Mirkin *Science* **283**, 661 (1999).

Y7.21

CONTROLLED DEHYBRIDIZATION OF DNA OLIGO-NUCLEOTIDES BY INDUCTION HEATING OF COVALENTLY LINKED Au NANOCRYSTALS. Kim Hamad-Schifferli, Media Lab; Jianping Shi, Center for Biomedical Engineering; Shuguang Zhang, Center for Biomedical Engineering; Jay Schwartz, Engeneos; Joseph M. Jacobson, Media Lab, MIT, Cambridge, MA.

The authors present experimental results on controllable dehybridization of DNA oligonucleotides by induction heating. The oligos are covalently linked to gold nanocrystals which can be inductively heated. By placing the sample in an alternating magnetic field, eddy currents are induced in the nanocrystals. Because the field and the induced eddy currents are alternating, the nanocrystals heat rapidly. Oligonucleotides covalently linked to the nanocrystals can be heated to dehybridize from their complements. Induction heating can rapidly dehybridize DNA oligos, on the timescale of a few seconds. The authors show results that the induction heating is not global but selective, meaning that one has the ability to heat oligos that are gold labeled but not those that are unlabeled, even if they are present in the same solution. Applications of this technique in biomedicine and computing will be discussed.

SESSION Y8/AA9: JOINT SESSION
NANOPATTERNING OF ASSEMBLED SYSTEMS
Chairs: Marie Angelopoulos and Elizabeth A. Dobisz
Thursday Morning, November 29, 2001
Back Bay D (Sheraton)

8:45 AM *Y8.1/AA9.1

DIFFUSION OF ALKANETHIOLS IN NANOPATTERNING. P.E. Sheehan, L.J. Whitman, Naval Research Laboratory, Washington, DC.

The patterning of alkanethiols has become a cornerstone in the burgeoning field of nanotechnology. Several patterning techniques have been developed, the more popular of which include stamping using polymeric masters, known as microcontact printing (mCP) and, more recently, the direct writing of the thiols using an AFM tip, known as Dip Pen Nanolithography (DPN). Importantly, in both techniques, diffusion of the thiol away from the contact area fundamentally limits the spatial resolution obtained. Obtaining the highest resolution possible from these techniques will require a full understanding of the rate and nature of thiol diffusion. To address this need, the radii of octadecanethiol spots deposited via DPN were studied as a function of tip-surface contact time and relative humidity. The increase in spot size with time was well described by two-dimensional radial diffusion from a constant source of finite radius. Fits using this formula revealed a diffusion constant of approximately 250 nm²/s with little dependence on humidity. Analysis of published images showing the spread of hexadecanethiol on gold after microcontact printing leads to comparable diffusion constants. Significantly, these values are four orders of magnitude smaller than that expected for diffusion through a bulk fluid such as water. Finally, the role of the water meniscus in DPN will be discussed.

9:15 AM Y8.2/AA9.2

DIRECTED ASSEMBLY OF ONE-DIMENSIONAL NANOSTRUCTURES INTO INTEGRATED DEVICE ARRAYS. Yu Huang, Charles M. Lieber, Harvard Univ, Dept of Chemistry, Cambridge, MA.

There have been increasing interest in using one-dimensional nanostructures as building blocks for bottom-up assembly of nanoscale electronics because they may serve both as wiring and critical device elements in future device architecture. A number of electronic and optoelectronic devices have been demonstrated using nanotubes or nanowires as the building blocks so far. The major challenge has been how to organize these one-dimensional nanostructures into integrated device arrays. Here we present a rational approach based on fluidics for the hierarchical assembly of one-dimensional nanostructures into well-defined functional networks.

We show that nanowires can be assembled into parallel arrays with control of the average separation, and by combining fluidic alignment with surface patterning techniques that it is also possible to control periodicity. In addition, complex crossed nanowire arrays can be prepared using layer-by-layer assembly with different flow directions for sequential steps. Transport studies show that the crossed nanowire arrays form electrically conducting networks, with individually addressable device function at each cross point. Lastly we will show that these parallel and orthogonal nanowire arrays can be used to construct integrated logic and memory device arrays.

9:30 AM Y8.3/AA9.3

SELF-ASSEMBLY PATTERNING OF COBALT DISILICIDE-NANOSTRUCTURES USING LOCAL STRESS EFFECTS. P. Kluth, Q.-T. Zhao, S. Winnerl, S. Lenk and S. Mantl, Forschungszentrum Jülich, Institut für Schichten und Grenzflächen (ISG-IT), Jülich, GERMANY.

We show a new self-assembly patterning method for generating epitaxial cobalt disilicide-nanostructures with dimensions down to 30 nm. This technique is based on anisotropic diffusion of Co/Si-atoms in a strain field during rapid thermal processing. The strain field is generated along the edges of a mask consisting of 20 nm SiO₂ and approximately 300 nm Si₃N₄. This mask, which is similar to that of the well known LOCOS process, is patterned with conventional optical lithography and dry etching. Single-crystalline CoSi₂-layers grown by molecular beam allotaxy (MBA) on Si(100) or ultra-thin silicon on insulator (SOI) substrates were patterned using this technique. During rapid thermal oxidation (RTO) of the masked silicide structure, a well defined separation of the silicide layer forms along the edge of the mask. These highly uniform gaps are as narrow as 40 nm. Combining this process with selective underetching of the SiO₂ underneath the mask and/or silicide/silicon etching delivers highly uniform CoSi₂ nanowires with diameters down to 50 nm. In addition, two parallel nanowires with a distance of 30 nm were achieved. Overlapping stress fields of two mask edges were used to generate 80 nm wires. The same masking technique was used to create nanogaps during the silicidation reaction forming epitaxial CoSi₂ in a titanium oxide mediated epitaxy process. Here, the mask was deposited on a Co/Ti/SiO₂/Si-structure. Subsequent rapid thermal annealing in forming gas (90% N₂, 10% H₂) leads to the formation of epitaxial CoSi₂ with a gap of approximately 100 nm along the edge of the mask. Simulations to estimate the stress profile generated by the nitride/oxide mask using an ATHENA process simulation tool were performed and are in agreement with our patterning results. The generated structures were used as building blocks for the fabrication of nanoscale MOSFET devices.

9:45 AM Y8.4/AA9.4

INTELLIGENT POLYELECTROLYTE MULTILAYERS: pH-RESPONSIVE DEPOSITION/REMOVAL OF THE MULTILAYER THIN FILMS AND THEIR MICRO-PATTERNING. Sung Yun Yang, Michael F. Rubner, Massachusetts Institute of Technology, Dept of MS&E, Cambridge, MA.

Recently, we have succeeded to build up multilayer films via the layer-by-layer (LBL) technique using hydrogen bonding. Polyacrylamide (PAAm) was used as a non-ionizable polymer, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) were used as hydrogen bonding partners. Multilayers were prepared by alternate dipping of glass or silicon substrates into the dilute polymer solutions at pH 3. At this pH, most of the carboxylic acid groups exist in the non-ionized form, and are available for hydrogen bonds. The key of this experiment was controlling the pH of all solutions including the solutions used in the rinsing steps in the process. The multilayers are stable at low pH and dissolved at high pH. Importantly, at physiological condition (pH 7.2, phosphate buffered solution) these multilayers dissolved into the buffer solution within a minute. This pH change breaks hydrogen bonds between layers by generating negative charges in the ionizable polymer (PAA and PMA). Thermal treatment of these multilayers, which results in a partial cyclic anhydride formation between carboxylic acid groups in the polymer chains, gives the multilayer a good stability at high pH. FTIR spectroscopy experiments confirm there is a high level of hydrogen bonding between amide and acid groups. Ellipsometry and quartz crystal microbalance (QCM) data of the multilayers with different molecular weights of PAAm were taken. In addition, cell adhesion to these multilayers was studied. Using the pH-dependent stability and UV-curable ability of the multilayers, we have succeeded in micro-patterning the films by ink-jet printing and photolithography. This type of multilayer system has a great potential in nanopatterned materials as well as in drug delivery.

10:30 AM Y8.5/AA9.5

NANOCONTACT PRINTING OF PATTERNED SUBMICRON FEATURES OF SELF-ASSEMBLED THIOL DERIVATIZED POLYMERS. John F. Rabolt, Mei-Wei Tsao, Jianling Li, University of Delaware, Dept. of Materials Science and Engineering, Newark, DE.

Microcontact and nanocontact printing have been used to produce patterned self-assembled monolayers (SAMs) and self-assembled polymers (SAPs) on a variety of substrates such as gold, silver or glass. In this technique, an elastomeric stamp, fabricated from poly(dimethylsiloxane) (PDMS) using a polymer master is wetted with an ink made of a solution of a thiol derivatized polymer. The polymer is then transferred by conformal contact to a substrate. In this talk, we will describe the formation of PDMS stamps from commercially available read-write compact disks (master) that have already been patterned with submicron features. SAMs and SAPs were then deposited on gold surfaces using submicron contact printing and micromolding techniques. Utilizing an atomic force microscope (AFM), these patterned surfaces were characterized and analyzed to determine the fidelity and aspect ratio of the features produced. Polarized FTIR measurements were made on the 5.5 nm. thick transferred polymer films in order to assess the extent of polymer orientation induced by the stamping process.

10:45 AM Y8.6/AA9.6

NANOPATTERNING 2D METALLIC SURFACES BY SOFT LITHOGRAPHY. Muhammet S. Toprak, German Salazar-Alvarez, Do-Kyung Kim, Maria Mikhailova, Mamoun Muhammed, Royal Institute of Technology, Dept of Materials Science and Engineering, Materials Chemistry Div, Stockholm, SWEDEN.

The fabrication of large areas of structured surfaces with feature sizes in the nanometer regime is still a challenge. Modern approaches to structure surfaces in sub-micrometer range involve the use of lithographic techniques, which have limitations regarding the minimum feature size. Nanostructures are made by imprinting methods, in which microcontact printing (μ CP) uses an inked patterned stamp to direct chemical reactions between molecules from the ink and the surface of a substrate. In this study, we report on the development of μ CP technique where the ink used on the surface of the stamp is made of alkanethiol solutions. Si was used as substrate on which self assembled monolayer of nanoparticles was formed at the contact regions. The stamps for μ CP are prepared from polydimethylsiloxane (PDMS) by polymerizing on a master defined by self-assembled colloidal SiO₂ nanosphere surfaces. The regions of contact subsequently used for deposition of metal nanoparticles resulting in 2D patterned metallic surfaces. By changing the size of nanospheres used in the master, it is possible to control the size and distance between contact points, i.e. metal deposited points, on the substrate. The chemical and physical properties of the system are investigated where the printed substrates were characterized by SEM and atomic force microscopy (AFM) technique and deposited particles were characterized by XRD.

11:00 AM Y8.7/AA9.7

FIELD INDUCED PATTERNING OF MECHANICALLY CONFINED POLYMER FILMS. David G. Bucknall, Department of Materials, University of Oxford, UNITED KINGDOM.

At elevated temperatures polymer films on a non-wetting solid surface form quasi-periodic patterns resulting from film rupture and dewetting [1]. This behaviour can be prevented by mechanically confining the film by a capping layer of, for instance SiO_x, to produce a completely different morphology [2]. This paper presents results of our recent studies on the morphological changes which occur to such mechanically confined films when an electric field is applied normal to the film thickness. An electric field applied across a polymer film with a free surface is known to produce structures which are either columnar or replicate the topography of the electrode [3]. By capping the polymer film with a thin metal layer, we produce very different structures. The effect of applying an electric field to these capped polymer films during annealing at elevated temperatures for a few minutes is to produce lateral morphologies which display both anisotropic, highly linear regions as well as areas which are totally isotropic. The effect the polymer film and capping layer thickness and field strength have on the resultant structures will be presented.

[1] G. Reiter; Phys. Rev. Lett.; 68(1), (1992), 75.

[2] K. Dalnoki-Veress, J.A. Forrest and J.R. Dutcher; Phys. Rev. E; 57(5), (1998), 5811.

[3] E. Schaffer, T. Thurn-Albrecht, T.P. Russell and U. Steiner; Nature; 403(6772), (2000), 874.

11:15 AM Y8.8/AA9.8

PLANAR MOLECULAR AND MACROMOLECULAR GRADIENTS: PREPARATION AND PROPERTIES. Jan Genzer, Kirill Efimenko, Tao Wu, Dept of Chemical Engineering, NC State University, Raleigh, NC.

Deposition of self-assembled monolayers (SAMs) offers one of the highest quality routes of systematically tuning the surface properties of materials: by controlling the chemical composition of the terminal group, the length, and microstructure of the SAM molecule, the

chemical and physical properties, including wetting, adhesion, friction, and biosensing, can be successfully tailored. While early studies concentrated mainly on preparing substrates with laterally homogeneous SAMs, recent advances in the field allowed for creating SAMs with two-dimensional chemical patterns. In particular, the microcontact printing (μ CP) technique has proven to be a convenient method for producing chemically patterned substrates. While μ CP is useful for decorating materials substrates with a variety of motif shapes and dimensions, it always produces sharp boundaries between the distinct chemical substrate regions. However, for some applications, it is required that the wetting properties of the substrate change gradually over a certain region in space. This situation can be accomplished by producing surfaces with a gradually varying chemistry along their length. In these so-called gradient surfaces, the gradient in surface energy is responsible for a position-bound variation in physical properties, most notably the wettability. Such gradient surfaces can be particularly useful to study interactions in biological systems, as the influence of the entire wettability spectrum upon protein adsorption or cellular interactions can be obtained in one single experiment. In our presentation we will discuss several methodologies of preparing planar molecular and macromolecular gradients on substrates. We will show that the gradient properties (including the wettability change and chain orientation) can be elucidated by a combination of several complementary experimental tools, including NEXAFS, static and dynamic contact angle measurement, spectroscopic ellipsometry, and FTIR. Moreover, we will demonstrate that the gradient properties (including steepness, position of diffusing front, and wettability) can be fine-tuned by forming the gradients on a flexible (and thus deformable) substrate, such as an elastomeric network.

11:30 AM Y8.9/AA9.9

SOFT CONDENSED MATTER NANO- AND MESOSCOPIC PATTERNS ON SEMICONDUCTOR SURFACES. V. Samuilov, Y.-S. Seo, Department of Materials Science, SUNY at Stony Brook, Stony Brook, NY; V. Ksenevich, Department of Physics, State University of Belarus, Minsk, BELARUS; J. Galibert, Laboratoire National des Champs Magnetiques Pulses, Toulouse, FRANCE; J. Sokolov, M. Rafailovich, Department of Materials Science, SUNY at Stony Brook, Stony Brook, NY.

The most striking property of soft condensed matter is the ability to self-organize - to create spatially oriented or periodic states on nano- and mesoscopic scale [1]. A novel and simple approach of self-organized fabrication of two dimensional mesoscopic networks with the feature size down to 50 nm has been developed. The technique is based on the self-organized patterning in a thin layer of complex liquid (polymer solution) in the presence of humid atmosphere. Two dimensional mesoscopic honeycomb-shaped carbon structures were produced by high temperature annealing of nitrocellulose precursors [2]. The polymer network was also utilized as a mask for further reactive ion etching of surfaces with epi-layer of GaAs [3,4] and GaAs/AlGaAs d-doped heterostructures [5]. These structures can be considered as regular arrays of mesoscopic cells or 2-D photonic band gap crystals. We have used diblock-copolymer system, self-assembled with L-B technique, to produce nano-patterns. These structures were utilized as templates for introducing metal nanopatterns on semiconductor surfaces by reactive ion beam etching for magnetic storage systems [6] and DNA separation on a flat surface [7] devices. DNA molecules positioning on Si surface by simple physical alignment process has been developed. The capillary forces applied by the receding front of the evaporating drop containing DNA molecule were used to align them perpendicularly to the direction of drying front. This alignment was used as a precise DNA molecules loading technique on Si surface in a new method of DNA separation [7]. We determined the resolution related to loading width by the thickness of the line, which was approximately equal to the length of the stretched DNA molecules.

1. T.A. Witten, Insights from soft condensed matter, Review of Modern Physics, 71, p.p. S367-S273, 1999.

2. V.A. Samuilov, J. Galibert, V.K. Ksenevich, V.J. Goldman, M. Rafailovich, J. Sokolov, I.A. Bashmakov, V.A. Dorosinets, Magnetotransport in mesoscopic carbon networks, Physica B, 294-295, p.p.319-323, 2001.

3. V.A. Samuilov, I.B. Butylina, L.V. Govor, V.K. Ksenevich, I.A. Bashmakov, I.M. Grigorieva, L.V. Solovjova, Fabrication of regular mesoscopic networks of GaAs wires, Superlattices and Microstructures, 25: (1-2) p.p.127-130, 1999.

4. V.A. Samuilov, I.B. Butylina, V.K. Ksenevich, G. Kiss, G. Remenyi, Observation of transport in mesoscopic honeycomb-shaped networks, Superlattices and Microstructures, 25: (1-2) p.p.197-202, 1999.

5. J. Galibert, V.A. Samuilov, V.K. Ksenevich, M. Rafailovich, J. Sokolov, Magnetoresistance of low dimensional mesoscopic honeycomb-shape GaAs networks, Physica B, 294-295, p.p.314-318, 2001.

6. S. Zhu, R.J. Gambino, M.H. Rafailovich, J. Sokolov, S.A. Schwarz, and R.D. Gomez, "Microscopic Magnetic Characterization of

Submicron Cobalt Islands Prepared Using Self-Assembled Polymer Masking Technique," IEEE Trans. Magn., 33, 3022, 1997.
7. N. Pernodet, V. Samuilov, K. Shin, J. Sokolov, M.H. Rafailovich, D. Gersappe, B. Chu, DNA Electrophoresis on a Flat Surface, Physical Review Letters, 85, p.p.5651-5654, 2000.

SESSION Y9: FABRICATION OF ORDERED
MAGNETIC NANOSTRUCTURES

Chairs: Elizabeth A. Dobisz and Leonidas E. Ocola
Thursday Afternoon, November 29, 2001
Back Bay D (Sheraton)

1:30 PM *Y9.1

MAGNETIC INTERACTIONS IN SELF-ASSEMBLED NANOPARTICLE ARRAYS. Dorothy Farrell, Saeki Yamamuro, Sara Majestic, Carnegie Mellon Univ, Dept of Physics, Pittsburgh, PA.

Monodisperse, surfactant-coated nanoparticles self-assemble into two- and three-dimensional arrays rather than chains because the dispersion forces dominate. However, magnetic interactions between particles have significant consequences in terms of the magnetic properties of the arrays. We briefly review the behavior of isolated monodomain particles and superparamagnetism. Using the bulk ferromagnetic-to-paramagnetic transition as a guide, we introduce the idea of a superparamagnetic-to-superferromagnetic transition. To study this experimentally, magnetic nanoparticle arrays with different particle sizes and separations are fabricated and characterized by SQUID magnetometry. Each sample is compared with a dilute sample of the same particles, in order to differentiate the contributions of interactions between magnetic particles. The temperature dependence of the remanent magnetization M_r reveals the Blocking temperature TB for isolated monodomain particles, and the critical temperature T_c for the superparamagnetic-to-superferromagnetic transition in the arrays. The results for different particle separations are compared with the predictions of magnetostatic and Anderson superexchange models. Hysteresis loops for the arrays with the applied field both in-plane and out-of-plane are compared with those for the dilute samples. The experimental values of the average local field are related to mean field theory calculations to understand collective switching behavior, and the requirements for switching particles independently.

2:00 PM *Y9.2

LARGE SCALE PERIODIC MAGNETIC NANOSTRUCTURES FABRICATED BY OPTICAL INTERFERENCE LITHOGRAPHY. A. Carl, S. Kirsch, and E.F. Wassermann Gerhard-Mercator-Universität Duisburg, Tieftemperaturphysik, Duisburg, GERMANY.

We report on the fabrication and on the magnetic properties of large scale periodic arrays of magnetic nanostructures consisting of Co/Pt multilayer dots with perpendicular magnetic anisotropy. The multilayered nanostructures are prepared on Si-substrates by alternating electron beam evaporation of Co and Pt onto periodically patterned photoresist masks under UHV conditions. The resist masks are fabricated by optical interference lithography utilizing Ar ion lasers with wavelengths of 457nm and 244nm, respectively. This allows for the fabrication of Co/Pt dot arrays with periodicities ranging from 125nm to 1000nm. The dot diameters can be adjusted between 60nm and 600nm. The final periodic dot-arrays cover an area of about 20cm² providing a maximum dot density of currently 41x10⁹dots/in². The global magnetic properties of these periodic dot-arrays are determined from magneto-optical Kerr effect measurements in polar geometry. The micromagnetic properties of single magnetic dots are investigated with quantitative magnetic force microscopy (QMFM) in external magnetic fields of up to $B = 0.1T$ perpendicular to the sample plane. Recently, we have developed a technique to calibrate the magnetic properties of magnetic force microscope tips. Using these calibrated tips allows one to conduct quantitative MFM measurements on the micromagnetic properties of single domain magnetic dots with perpendicular magnetic anisotropy. The method is demonstrated for single domain Co/Pt dots for which QMFM is employed to measure the hysteresis loop and coercivity as well as the z-component of both, the magnetization and the stray field on a sub-100nm scale, supported by the German BMBF.

2:30 PM Y9.3

HIGH DENSITY HEXAGONAL NICKEL NANOWIRE ARRAYS WITH 65 AND 100 NM-PERIOD. Kornelius Nielsch, Ralf B. Wehrspohn, Jochen Barthel, Jürgen Kirschner, and Ulrich Gösele, Max-Planck-Institute of Microstructure Physics, Halle, GERMANY; Saskia F. Fischer and Helmut Kronmüller, Max-Planck-Institute of Metal Research, Stuttgart, GERMANY; Thomas Schweinböck and Dieter Weiss, Institute of Applied Physics, University of Regensburg, GERMANY.

We demonstrate the application of nickel nanowire arrays for perpendicular magnetic storage media with areal densities beyond the superparamagnetic limit (>70 Gbit/in²). Highly ordered alumina pore channel arrays are used as templates for the fabrication of magnetic nanowire arrays. These well-defined templates are based on an approach by Masuda and Fukuda [Science 1995, 268, 1466] and have an interpore distance of 65 and 100 nm and a monodisperse pore diameter of ≈ 30 nm. The pore channels are hexagonally arranged in 2D-domains, which extend over more than ten interpore distances. For the first time, nearly 100% metal filling of the alumina pore structures is obtained by a novel pulsed electrodeposition technique. Due to the high ordering degree of the nanowires arrays, we detect a squareness of $\approx 100\%$ and coercive fields of 1200 Oe in the direction of the nanowires. This is the highest coercivity reported for high-density Ni nanowire arrays. Furthermore, the homogeneous metal filling allows detailed investigations by complementary magnetic characterization methods such as magnetic-force-microscopy (MFM) or Brillouin light scattering experiments. The MFM measurements have been carried out by applying magnetic fields on magnetized and demagnetized samples to study the switching behavior of individual nanowires inside the arrays. Magnetic wires have been locally switched by a strong MFM tip and a variable external magnetic field. The MFM results show a good agreement with the bulk magnetic hysteresis loops and magnetic simulations. Additionally, we will show preliminary results on the fabrication of magnetic nanowire arrays with a quasi 2D-monocrystalline arrangement of the nanomagnets. To force the self-assembly during the formation of the templates e-beam lithography is used. This pre-structuring method enforces a monocrystalline arrangement of the pore channels.

2:45 PM Y9.4

MAGNETIC DOT ARRAYS FABRICATED USING BLOCK COPOLYMER LITHOGRAPHY. Joy Y. Cheng, Caroline A. Ross, Edwin L. Thomas, Dept of Materials Science and Engineering, Cambridge, MA; Rob G.H. Lammertink, Mark A. Hempenius, G. Julius Vancso, Dept of Materials Science and Technology of Polymers, University of Twente, AE Enschede, THE NETHERLANDS.

Large area high-density magnetic dot arrays of cobalt and permalloy (NiFe) are fabricated using self-assembled block copolymer lithography. The fabrication process consists of consecutive pattern transfer processes from a block copolymer layer to an oxide intermediate layer, a tungsten hard mask layer, and finally to a magnetic thin film layer. In this fabrication scheme, the size, aspect ratio and intrinsic magnetic properties of the magnetic dot arrays are adjustable by varying the size and composition of the block copolymer layer, which defines the pattern, and the thickness and composition of the magnetic layer. Polystyrene (PS)-*b*-polyferrocenyldimethylsilane (PFS) with various molecular weights is used as a self-assembled mask. When spun onto a surface, the PFS forms a layer of spheres inside the PS matrix, and the PS can then be removed in an oxygen plasma to leave a PFS template that ultimately defines the magnetic dots. Close-packed arrays of 5 to 15 nm thick magnetic dots with diameters from 15 nm to 25nm and spacings from 30nm to 50nm were produced by ion-milling Co or NiFe evaporated films. Despite their small size, the Co dots are ferromagnetic at room temperature but show strongly temperature- and time-dependent magnetic properties. For example an array of 20 nm diameter, 8 nm thick Co dots at 300K had an in-plane coercivity of 70 Oe measured at a sweep rate of 5 Oe/s but a coercivity of 76 Oe measured at 500 Oe/s using an alternating gradient magnetometer, indicating that thermal energy significantly promotes magnetization reversal. In this paper the fabrication process will be discussed, including methods to control the perfection and orientation of the self-assembled template. The time- and temperature-dependent magnetic properties of these single domain particles will be discussed as a function of size and shape.

3:30 PM *Y9.5

SELF-ASSEMBLED STRUCTURES OF GAS-PHASE PREPARED Fe-Pt NANOPARTICLES. Bernd Rellinghaus, Sonja Stappert, Mehmet Acet, and Eberhard F. Wassermann, Experimentelle Tieftemperaturphysik, Gerhard-Mercator-Universität, Duisburg, GERMANY.

We report on a nonlithographic method for the preparation of self-assembled stoichiometric Fe-Pt nanoparticles via inert-gas condensation utilizing a DC sputtering system. Prior to being deposited onto amorphous carbon substrates the particles pass a sintering stage, where they are subjected to temperatures of up to $T_S = 1000^\circ C$. Particles, which pass the sintering stage at room temperature (RT), display irregular shapes, thus indicating that they are not yet thermally equilibrated. On the other hand, particles, which are sintered at elevated temperatures of $T_S = 600^\circ C$, display a regular faceting. High resolution transmission electron microscopy (HRTEM) reveals that these particles are mostly of icosahedral structure and thus have an almost spherically symmetric shape. The deposited Fe-Pt nanoparticles exhibit a relatively high mobility on the

amorphous carbon support. In particular, the high-temperature sintered particles are found to form patches of hexagonal close packed patterns via self-assembly on the substrate. Particles within such a pattern do not touch one another but are separated by some 1.5nm, though these particles do not wear any coating. The observed inter-particle separation is ascribed to the formation of carbon wells on the underlying amorphous carbon film. In case of the RT-sintered particles, the irregular non-equilibrium morphology seems to impede the pattern formation.

4:00 PM Y9.6

MAGNETIC PROPERTIES OF THREE-DIMENSIONAL PERIODIC NANOSTRUCTURES. L. Sun, Department of Materials Science and Engineering, C.L. Chien, Department of Physics and Astronomy, P.C. Searson, Department of Materials Science and Engineering, The Johns Hopkins University, MD.

Nanoporous magnetic structures with three dimensional periodicity have been fabricated by electrodeposition into self-assembled colloidal templates. Although ordered structures can be fabricated by conventional thin film processing, sequential deposition and lithography over many layers is time consuming. In contrast, the assembly of colloidal crystals to form ordered structures many layers thick can be achieved in a single processing step. In this work, latex microbeads are self-assembled to form periodic, closed packed templates. Three-dimensional ferromagnetic structures with nanometer scale periodic features are formed in these templates by electrodeposition. The magnetic properties of these 3D nanostructures are reported.

4:15 PM Y9.7

HIGH-DENSITY MAGNETIC DOT AND ANTI-DOT ARRAY FABRICATION VIA NANOSPHERE PHYSICAL MASKS. G.C. Spalding, Paul Curran, Brad Andrews, Illinois Wesleyan Univ, Dept of Physics, Bloomington, IL; J.E. Elenewski, Univ of Illinois, Dept of Physics, Urbana, IL.

We discuss non-lithographic means of controlling the assembly of nanoparticles onto a substrate. Following the work of Xia's group [1], we describe the construction of uniform microfluidic cells which may be used to encourage a collection of monodisperse, mesoscale particles to form large-scale, ordered colloidal crystals. In our work, cells are designed to form monolayers and bilayers. We discuss the use of these monolayers and bilayers as physical masks during the deposition of metals, in order to produce high density, ordered dot arrays [2]. We also introduce the use of such masks in the production of anti-dot arrays. That is, once assembled, the colloidal monolayers or bilayers can serve as a physical mask, selectively protecting areas of the underlying substrate from either physical vapor deposition or from a reactive plasma. Because the clear, line-of-sight channels between the masking particles are much smaller than the particles themselves, extremely fine features can be transferred to the substrate. This novel technique for high-density nanopatterning is inexpensive, can work on curved surfaces, and over extremely large areas. We discuss details of the fabrication, the tunability of feature sizes, and a variety of applications.

[1] S.H. Park, Y. Xia, *Langmuir* 15, 266 (1999).

[2] J.C. Hulteen, et al., *J. Phys. Chem. B.* 103, 3854 (1999).

4:30 PM Y9.8

FABRICATION OF NANOPERIODIC SURFACES STRUCTURES BY ETCHING OF DISLOCATION ARRAYS IN TWIST-BONDED BICRYSTALS. Fang Mei, Martin J. Murtagh, Stephen L. Sass, Cornell University, Dept. of Materials Science and Engineering, Ithaca, NY; Rikard A. Wind, Yu Wang, Melissa A. Hines, Cornell University, Dept. of Chemistry, Ithaca, NY.

The smallest lateral feature on commercial microprocessors is currently 150 nm, while the distance between binding sites on a human antibody is ~10 nm. Nanofabrication at biologically important length scales is expected to remain beyond the capability of commercial lithography for the foreseeable future. A new method for the fabrication of periodic arrays of surface features with controlled spacing of 2 - 100 nm will be described in this paper. Our approach is based on the two-dimensionally periodic screw dislocation array that occurs at the interface between two single crystal substrates twist-bonded at a misorientation angle θ to form a bicrystal. The desired periodic structure is brought to the surface by a dislocation etch. The spacing, d , between the dislocations (and the features of the surface structure) is related to θ by Frank's rule, $d = |b|/2\sin(\theta/2)$, where b is the dislocation Burgers vector. The feasibility of this approach will be demonstrated. A Si bicrystal was formed by twist-bonding a Si (100) wafer to a 100 nm thick Si (100) single crystal film that is part of a commercial silicon-on-insulator (SOI) wafer. After removal of the Si handle crystal and thin silicon dioxide film, the upper thin crystal of the bicrystal was etched. Atomic force microscopy showed periodic surface features with spacing of 38 nm, in

good agreement with the chosen θ . Periodic spacings between 100 nm and 2 nm can be generated by varying θ between 0.2 degree and 10 degree. Such nanopericodic structures have a variety of electronic, magnetic storage and biological applications.