

SYMPOSIUM C

Innovations for Sub-100nm Lithography–Materials and Processes

November 29 - December 1, 2004

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* Invited paper

8:30 AM *C1.1

Directed Self-Assembly of Imaging Materials for Nanoscale Lithography. Paul F. Nealey and Juan de Pablo; Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin.

Current high-resolution lithographic processes are based on chemically amplified resists (CARs) and are routinely used to pattern features with dimensions less than 100 nm. As feature dimensions shrink to below 50 nm, however, the use of CARs poses significant new challenges with respect to problems such as line edge roughness, critical dimension control, and collapse of patterned structures due to capillary forces. Our research seeks to explore and develop new materials and processes for advanced lithography in which self-assembling materials are integrated into existing manufacturing processes to deliver molecular level control. Essential attributes of current manufacturing practices, pattern perfection, exacting tolerances and margins, and placement of the structures, including registration and overlay, with nanometer precision, are retained. A key strength of our approach to investigate directed assembly at the nanoscale is to employ a combination of experiment, molecular simulation, and theory. In one strategy, we are investigating imaging materials based on patterned polymer brushes. The principal concept of the new imaging materials is that surface energy provides the means to achieve nanoscale features with atomically smooth sidewalls. Experiment and molecular simulation show that the dimensions, shapes, and contours of the features depend on the molecular weight and the grafting density of the brushes. In a second strategy, we integrate the self-assembly of thin films of block copolymers with advanced lithography to induce the epitaxial assembly of densely packed nanoscopic domains on chemically nanopatterned substrates. The areas over which the patterns are defect free, oriented and registered with the underlying substrate are arbitrarily large, determined by the size and quality of the lithographically defined surface pattern rather than the inherent limitations of the self-assembly process, and the process latitude depends on the nature of the interfacial interactions between the patterned substrate and the blocks of the copolymer. The structure of the films can be described and predicted from a combination of Monte Carlo simulations and theory.

9:00 AM C1.2

NanoContact Printing: A Technique for Replicating Multi-component Nanoscale Devices in a Single Printing Cycle. A. Amy Yu and Francesco Stellacci; Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

The recent interest in nano-science has catalyzed research in the development of nano-fabrication techniques. New highly versatile nanolithography techniques based on scanning probe microscopes have been reported. A wide variety of organic and inorganic substrates can be patterned either by inducing localized chemical modifications or by forming self-assembled monolayers (SAMs). Unfortunately, they all have in common the same drawback: they are extremely slow. A new versatile method (NanoContact Printing, NCP) that will allow for the self-assembly mediated stamping of nanofabricated substrates will be presented. Patterns generated by any nanofabrication technique could be used as stamps. In general this method will be based on a four-step approach: 1) A patterned SAM of single-strand-DNA terminated molecules is formed. 2) Complement DNA strands are assembled on the patterned DNA SAMs. The complement DNA is functionalized on one end (the one that is far from the substrate) with a chemical moiety able to react with a surface (e.g. thiol/gold or siloxane/glass). 3) A second substrate is brought close to the first, allowing for the formation of chemical bonds between the reactive groups on the complement DNA and the substrate surface. 4) The DNA double helices are dehybridized by mild heating (40-60 °C depending on DNA length). The two substrates are then separated. After this process the first substrate is left in its initial state and the second is a replica of the first one, exactly what is needed for a stamping technique. One of the main advantages of this method is that multiple DNA strands (each encoding different information) can be printed at the same time, thus allowing for a complex chemical pattern to be formed. The parallel printing of a pattern formed by four DNA strands will be presented. The resolution and fatigue property of this novel approach to printing soft materials will be presented and discussed. Finally, features written via Dip Pen Nanolithography have been successfully reproduced using nanocontact printing, showing the possibility of integrating this printing methods with advanced scanning probe lithography techniques.

9:15 AM C1.3

Electron Beam Nanolithography and Unimolecular

Nanosheets Based on Aromatic Self-Assembled Monolayers. Wolfgang Eck¹, Armin Goelzhaeuser², Michael Grunze¹, Alexander Kueller¹, Andrej Shaporenko¹, Yian Tai¹ and Michael Zharnikov¹; ¹Applied Physical Chemistry, University of Heidelberg, Heidelberg, Germany; ²Physics of Supramolecular Systems, University of Bielefeld, Bielefeld, Germany.

When self-assembled monolayers of functionalized biphenyls and terphenyls on gold or silicon are irradiated with electrons, they are dehydrogenated and cross-linked and can be used as ultrathin negative resist. On silicon, resolutions of 20 - 40 nm for line gratings and 11 nm for single lines have been obtained after wet etching. Cross-linking initiates at the monolayer/ambient interface and exhibits a gradient within the monolayer, as angle dependent NEXAFS measurements show. The chemical composition of the monolayers remains unchanged, except for dehydrogenation of the aromatic units and reduction or cleavage of terminal substituents. The cross-linked SAMs can be released from the surface by chemical destruction of the anchor group or by dissolution of the substrate. Ultrathin free-standing sheets with the thickness of a single molecule and lateral dimensions in the micrometer range are obtained in this way.

10:00 AM *C1.4

Molecular Rulers: Advancing Nanolithography to Smaller Scales and Greater Precision. Paul S. Weiss¹, M. E. Anderson¹, E. M. Carter¹, M. W. Horn², A. R. Kurland¹, H. Tanaka¹ and G. N. Taylor¹; ¹Chemistry and Physics, The Pennsylvania State University, University Park, Pennsylvania; ²Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania.

We combine conventional lithographic techniques with chemical self-assembly for the creation of nanostructures whose spacing and edge resolution reach nanometer-scale precision. The controlled placement and thickness of self-assembled multilayers composed of alternating layers of complementary chemical pairs form precise "molecular ruler" resists to produce tailored, lithographically defined patterns. We have advanced the use of molecular rulers through a number of new and continuing strategies. We have demonstrated two methods of multilevel molecular ruler processing using photolithography, in order to show that these processes are compatible with conventional methods now used for device production. We have also explored non-conventional parent structures created by self-assembly processes both for producing nanostructures and for elucidating fundamental aspects of multilayer assembly as they apply to this method. We have also demonstrated the ability to make multiple generation and selectively positioned structures.

10:30 AM C1.5

Novel, Maskless, Etching-Free, Sub-100nm Patterning Process of Metal Oxide Using Polymeric Sub-Microstructure Templates. Myunghwan Kim¹, Shizhou Yang¹, Lynne A. Samuelson² and Jayant Kumar¹; ¹Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts; ²U.S. Army RDECOM, Natick Soldier Center, Natick, Massachusetts.

Relief structures were inscribed in a thin film of an azobenzene-functionalized polymer on a quartz substrate by irradiation with the appropriate wavelength of light. An array of V-shaped grooves was fabricated 1 μm-wide and 0.5 μm-deep. Sub-10 nm sized particles of metal oxides were deposited with polyelectrolytes onto the grooves by the ionic layer-by-layer deposition technique. The assembly was heated to a suitable temperature such that a parallel array of one dimensional metal oxide settled on the substrate after thermal degradation of the polymeric template. The height and width of the resulting nanowires was tunable from less than 100 nm to a micrometer with lengths longer than several hundred micrometers, depending on the amount of deposited metal oxide and the geometry of the polymeric templates. In addition, zero dimensional metal oxide structures were patterned using polymeric egg-crate-structure templates. This was done by writing twice at 90° angles in the polymer film. This process is both time and cost efficient and progress is ongoing in further developing the technique. These structures have been investigated using AFM, SEM, XPS, XRD, and TEM.

10:45 AM C1.6

Self-assembled monolayers creating tailored resists for nanostructure fabrication. Mary Elizabeth Anderson¹, Erin M. Carter¹, Adam R. Kurland¹, Charan Srinivasan², Mark W. Horn² and Paul S. Weiss¹; ¹Departments of Chemistry and Physics, Pennsylvania State University, University Park, Pennsylvania; ²Department of Engineering Science and Mechanics, Pennsylvania State University, University Park, Pennsylvania.

Chemical self-assembly in combination with lithographic processing can be used to define nanostructures with precise spacing and edge resolution reaching the nanometer-scale. Self-assembled multilayers,

composed of alternating layers of α,ω -mercaptoalkanoic acids and coordinated metal ions, are selectively deposited on initial lithographically defined gold structures. These multilayers form precise "molecular ruler" resists that can be tuned to a desired thickness, in the 5-100 nm range, based on the number of layers deposited. Then, metal is deposited on the sample and the resist is removed, yielding spacings between metal structures dependent on the tailored resist's dimensions. This approach has been demonstrated with nanostructures generated by electron beam and photolithography, as well as those based entirely on self-assembly.(1-3) This method has been advanced by automating the process, improving chemical lift-off, creating sacrificial structures, producing multiple generation structures, and selectively defining secondary structure placement.(1-3) Work is underway for designing and patterning complex nanostructures by exploiting methods of directed self-assembly to build molecular ruler resists with independently controlled materials and spacings. Molecular ruler resists can withstand the rigors of lithographic processing and are being developed to advance this method toward device fabrication. Basic device architectures that take advantage of the precise nanoscale spacings produced by this technique are in the initial stages of creation. (1) A. Hatzor and P. S. Weiss, *Science* 291, 1019 (2001). (2) M. E. Anderson et al., *J. Vac. Sci. Technol. B* 21, 3116 (2003). (3) M. E. Anderson et al., *Appl. Phys. Lett.*, submitted.

11:00 AM **C1.7**

Resist for Extreme UV Lithography: Chemical Amplifiable Silicon Polymers. Juan-Pablo Bravo¹, Young-Je Kwark¹, Heidi B. Cao², Hai Deng² and Christopher K. Ober¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Intel Corporation, Hillsboro, Oregon.

Advances in lithography pioneered by the semiconductor industry are driving new technologies based on microfabrication. At the same time, the goal of further improving microfabrication capabilities that can routinely achieve dimensions of less than 50 nm will require the design of new photopolymers and strategies using wavelengths as short as 13 nm (EUV). EUV lithography (EUVL) is a challenging emerging technology that has proven its feasibility to image small features, yet still requires improvement in key areas such as photoresists. Widely used elements, such as oxygen and fluorine, are highly absorbing at 13 nm making them undesirable for incorporation into EUV resists. Moreover, the requirement for chemical amplification is making the design more complex when selecting possible elements to be used in new polymer platforms. Our current efforts have focused on synthesizing polymers made from low x-ray absorbing elements, including C, H and Si. This paper discusses new developments in positive tone chemically amplified polysilane and polysilazanes designed for high resolution lithography. In these studies, highly transparent polysilanes and polysilazanes have shown promising results as resist materials. In this approach, polysilanes such as polymethylphenylsilane were selected as backbone structures for photoresist materials. Silicon has one of the lowest absorption cross sections at 13.4 nm making it a very transparent element for EUVL. However, the lack of contrast and sensitivity of polysilanes restricts their use in lithographic processes. This issue was overcome by the incorporation of an acid sensitive units, such as tert-butylacetyl, n-butylacetyl and tert-butylacetoxyphenyl chemical groups, into the polysilane backbone. This approach also resolves issues with insolubility in the developer solution. In a second approach, polysilsesquiazanes (polysilazanes in a ladder form) have also been studied as resist material for EUVL. This type of silicon polymer possesses chemical amplification attributes despite the lack of oxygen atoms. The physical properties of the polymers, including T_g, sensitivity, and solubility, could be tuned by using different substituents and varying the branching density. Their outgassing properties at 13.4 nm have also been evaluated. With the advent of EUV lithography standard resist materials will have difficulty fulfilling the new stringent patterning requirements and we believe our findings provide new insight in the search for effective EUV resists.

11:15 AM ***C1.8**

Electronics and Optoelectronics with Single Carbon Nanotube Molecules. Phaedon Avouris, Physical Sciences, IBM Research, Watson Research Center, Yorktown Heights, New York.

Carbon nanotubes (CNTs) are 1-dimensional nanostructures with unique properties that recommend them for applications in nanoelectronics and optoelectronics. I will discuss the electronic structure and electrical properties of semiconducting carbon nanotubes and the fabrication and performance of nanotube field-effect transistors. Transport experiments and simulations will be used to determine the switching mechanism of nanotube transistors, their scaling rules, the nanotube-metal interactions and the role of the ambient environment on their transistor properties. I will then discuss how these findings can be utilized to produce high performance p-, n-type nanotube field-effect transistors (CNTFETs) and logic circuits.

I will show that CNTFETs with very thin gate insulator films become ambipolar. In these devices, depending on the applied gate bias, both electrons and holes can be involved in electrical transport. While this behavior is undesirable in logic applications, it can be ideal for photonic applications. When electrons (e) and holes (h) injected from opposite terminals of a CNTFET meet, they recombine, and a fraction of these encounters releases the recombination energy in the form of light. Using this scheme we produce an electrically excited and controlled light emitter involving a single nanotube molecule. The radiative recombination nature of the emission is confirmed by measurements of its spectrum, its polarization, and the dependence of its intensity on applied bias. By spatially resolving the light emission from long nanotubes as a function of the applied bias, the interacting boundaries of the e- and h-currents can be visualized. The emission intensity provides information on the magnitude of the minority currents, the shape of the emitting spot gives their recombination length, while the emission line-widths provide information on the energy distribution of the carriers. We have also demonstrated the reverse process of recombination, i.e. the photogeneration of e-h pairs in the single CNT channel. The observed resonances in the photoconductivity spectra of individual CNTs correspond to the exciton states of the CNT. Thus, a single device, a CNT-FET, can act, depending on the applied biases, as a switch (transistor), a light emitter or a light detector.

SESSION C2/GG3: Joint Session: Emerging Paradigms in Nanopatterning and Mesoassembly
Chairs: Paul Braun, Eric Lin and G. Ramanath
Monday Afternoon, November 29, 2004
Room 311 (Hynes)

2:30 PM ***C2.1/GG3.1**

Mesoscale Architectures from Nanounits: Assembly, Fabrication. A. Paul Alivisatos, Chemistry, University of California, Berkeley, Berkeley, California.

This talk will focus on the use of creation of new shapes and topologies of nanocrystals. Nanocrystals can act as a fundamental unit for chemical transformation. For example, through studies of interdiffusion between two components in a particle, we have learned how to make hollow inorganic nanocrystals. A second example concerns controlled branching, which enables us to create new types of heterostructures. Finally, very recent work in which we employ cation exchange to alter the chemical composition of nanocrystals will be described.

3:00 PM ***C2.2/GG3.2**

The Future of The Semiconductor Industry: Top Down or Bottom Up? Ralph R. Dammel, AZ Electronic Materials, Clariant Corporation, Somerville, New Jersey.

The rapid rise of the semiconductor industry is without doubt one of the main success stories of modern industrial development. At the heart of the industry's success is its ability to keep shrinking device sizes exponentially over time according to Moore's Law, resulting in ever decreasing cost per function. As of today, the industry's Roadmap looks out 14 years, until 2018, without forecasting a slowdown of Moore's Law. From the technical side, we have a pretty good understanding what needs to be done to pattern the 45 nm features the Roadmap requires at the end of this decade, but there are still fundamental questions to be resolved for the years further out. In particular, some question whether the patterning capability of the chemical amplification mechanism (which underlies the dominant class of photoresists today) can be extended beyond 50 nm. Even if the technical hurdles are overcome, the investment cost of photolithography and manufacturing future chip generations in general may become so high that the market will be unable to bear it. Such an economic end to Moore's Law could occur even if it is technically feasible to make smaller devices and although the cost per function would continue to decrease. Following an outline of present-day photolithographic technology, this paper will explore a way out of the coming crisis that may lie in the use of some form of nanoimprint technology, which presently still is in an early stage but has the potential to be substantially cheaper than conventional photolithography.

3:30 PM ***C2.3/GG3.3**

Unconventional Nanofabrication and Meso-Scale Self-Assembly. George M. Whitesides, Logan McCarty, Qiaobing Xu, Byron Gates, Brian Mayers, Lara Estroff and Vijay Krishnamurthy; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Chemistry, with stimulus from biology, is beginning to develop a

range of new concepts for the fabrication of mesoscale systems by templated self-assembly from nanoscale components: these include a range of types of self-assembly, printing, molding, microfluidic patterning, electrochemistry, sectioning, and related techniques designed to make it possible to design complicated structures having electrical, optical, biological or magnetic functionality and to assemble and replicate these systems efficiently. These concepts suggest approaches to fabrication that are substantially different from photolithography in their areas of application.

4:00 PM *C2.4/GG3.4

Massively Parallel Dip Pen Nanolithography. Chad A. Mirkin, Chemistry, Northwestern University, Evanston, Illinois.

Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic nanoelectronics. This talk will describe the fundamental capabilities of DPN and its use to generate and study a wide variety of nanostructures using materials ranging from oligonucleotides to proteins to conjugated polymers. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

4:30 PM *C2.5/GG3.5

Nanoimprint Lithography (NIL), Laser-Assisted Direct Imprint (LADI) And Lithographically-Induced Self-Assembly (LISA). Stephen Y. Chou, Department of Electrical Engineering, NanoStructure Laboratory, Princeton University, Princeton, New Jersey.

The talk will present several innovative nanopatterning methods and their advancements developed at NanoStructure Lab at Princeton. The first is nanoimprint lithography (NIL), which patterns a resist by physical deformation using a mold. We will present our demonstration of sub-12 nm pitch, sub-5nm feature size, sub-20 nm alignment (one sigma), and large-area uniformity in NIL, as well as various NIL tools. The second is laser-assisted direct imprint (LADI), which directly patterns nanostructures on hard material surface, chemical-free and without etching. LADI uses an excimer laser, shining through a transparent mold, to melt a thin surface layer of a hard material, and then presses a mold into the molten material. We will show our achievements of sub-10 nm features imprinted in Si, LADI in SiC and metals (Au and Cu), and new applications of LADI in wafer planarizations. Finally, we will present lithographically-induced self-assembly (LISA), where self-assemblies of nanostructures are guided by much larger patterns and can achieve single domain over a large area. Furthermore, we used LISA to achieve self-alignments and self-assembly (SALSA) between the connections and electronic devices to create random access-electronic devices array. The work was supported in part by DARPA and ONR. The author acknowledges the contributions of other members of NanoStructure Lab at Princeton to the presentation materials.

SESSION C3: Semiconductor Fabrication Technology
Chairs: Marie Angelopoulos and Rod Kunz
Tuesday Morning, November 30, 2004
Republic A (Sheraton)

8:30 AM *C3.1

The Development of Immersion Lithography. Michael Switkes, Submicrometer Technology Group, MIT Lincoln Laboratory, Lexington, Massachusetts.

Immersion lithography has rapidly emerged as an important candidate for upcoming patterning applications with the potential to meet the needs of the semiconductor industry at the 45-nm node and even beyond. It has generated significant interest in the lithography community, and it is actively being evaluated as a potential technology for the 65 nm node and beyond, corresponding to expected insertion years of 2007 and later. We review the development and current challenges of immersion lithography, and describe ongoing work to meet these challenges. The novel element in immersion lithography is, of course, the liquid itself. While water appears to be the liquid of choice at 193 nm, much work remains in the development of suitable liquids for 157 nm. The major difficulty to date has been liquid absorbance. Starting with fluorocarbon materials having as-received absorbances $\alpha_{157} \approx 10 \text{ cm}^{-1}$, a combination of custom synthesis and, more importantly, careful purification, has pushed absorbances to 0.5 cm^{-1} and below. This allows a transmission of 90% at a 1 mm working distance, approaching the requirements of the

lithography tools. Other properties of the liquid, in particular its index of refraction and long-term compatibility with lens materials, are just now beginning to be examined. We are in the final stages of integrating a 157 nm immersion microstepper seen in figure 1. When complete, this 1.3 NA system with a 60 μm field will allow further development of 157 nm immersion compatible liquids, resists, and processes. We describe the design and construction of the microstepper as well as report on its current status. While immersion lithography at 193 nm appears promising, potential issues remain in several areas, some of which may also impact on 157 nm immersion. The first is the possibility of bubble formation in the immersion liquid. Since bubbles which are near the resist surface are particularly problematic for imaging, we have studied the possibility of bubble formation due to resist outgassing. Figure 2 shows an image of several micron sized bubbles formed from the laser induced outgassing of an APEX resist chosen especially for its high outgassing. We are conducting a survey of model and candidate 193 nm resists to determine their potential for producing bubbles. A second class of bubbles, so-called *nano-bubbles* with lateral dimensions on the order of 100s of nm, has been shown to form spontaneously at the interface of water with hydrophobic surfaces. Using a new technique, we have determined that these bubbles are due to the dissolved gas in the water and thus degassing should prevent their interfering with immersion lithography.

9:00 AM C3.2

Direct Measurement of the Water Distribution within an Immersed Model Photoresist. Bryan D. Vogt¹, Christopher L. Soles¹, Vivek M. Prabhu¹, Sushil K. Satija², Eric K. Lin¹, Wen-li Wu¹, Dario L. Goldfarb³ and Marie Angelopoulos³; ¹Polymers Division, NIST, Gaithersburg, Maryland; ²Center for Neutron Research, NIST, Gaithersburg, Maryland; ³T.J. Watson Research Center, IBM, Yorktown Heights, New York.

The emergence of immersion lithography as a potential alternative for the extension of current lithography tools will require a fundamental understanding of the interactions between the photoresist and the immersion liquid such as water. The water concentration depth profile within the immersed photoresist films supported on HMDS treated silicon wafers was measured with neutron reflectometry. The bulk of the polymer films swelled to the equilibrium water concentration, however a gradient in water concentration was observed near the polymer/HMDS substrate interface with a concentration of approximately 17 % by volume fraction and extending up to 50 Å into the film for the two polymer systems examined. Poly(4-hydroxystyrene) absorbs more than this amount and exhibits depletion near the interface, whereas poly(4-*tert*-butoxycarbonyl-oxystyrene) absorbs less and thus exhibits a water excess layer. As the total film thickness approaches this length scale, the substrate induced concentration gradients lead to a film thickness dependent swelling; enhanced or suppressed swelling is witnessed for the excess or depleted interfacial concentrations, respectively.

9:15 AM C3.3

Structure - Composition - Property Relations For Absorbance and Index of 157 nm Immersion Lithography Fluids. Roger H. French, Michael F. Lemon, Min K. Yang, Sheng Peng, Weiming Qiu and Robert C. Wheland; DuPont Central Research, Wilmington, Delaware.

157nm immersion lithography can enable optical lithography for the 32 nm half pitch nodes of the ITRS roadmap. For immersion lithography at 157 nm, the challenge is to develop a low absorbance, high index immersion fluid (IF) with an optical absorbance A/cm below 0.4, so as to permit a 1 mm working distance, and a high index so as to produce a low effective lithographic wavelength or a numerical aperture greater than 1. Selected fluorinated alkanes, amines, and ethers have been found to have adequate transparency. The prime structural requirement is short perfluoroalkane chains ($\text{C}_n\text{F}_{2n+2}$) or short perfluoroalkyl segments (C_nF_{2n}) alternating with oxygen, nitrogen, CFH, or CH₂ leading to bond alternation. It is important to distinguish intrinsic compound transparency from absorption by water, oxygen, other trace contaminants since even 1 ppm of the wrong impurity can contribute as much as 0.1 absorbance units/cm at 157 nm. Short chain perfluorinated and partially fluorinated alkanes, ethers, and amines typically have refractive indices ranging from 1.31 to 1.33 at 157 nm. A perfluoroether tested had a refractive index of 1.366 at 21 C. Ideally refractive index should be > 1.4 . Since the Kramers Kronig dispersion relations correlate the absorbance and the index of refraction of a material, the design of high index, low absorption fluids requires the consideration of the fundamental interatomic bonding and optical properties of materials. Using VUV spectra to 30 eV (40 nm) of prototypical polymers, coupled with lorentz oscillator models, gives insights into various strategies for achieving higher index, while maintaining low absorbance.

9:30 AM *C3.4

Metrology for Nanometer Scale Lithography.

Mark L. Schattenburg and Ralf K. Heilmann; Space Nanotechnology Laboratory Center for Space Research, MIT, Cambridge, Massachusetts.

Lithographic manufacturing processes are critically dependent on precise and accurate dimensional metrology. Although metrology research and development has traditionally taken a back seat to other more pressing issues such as lithography tools and materials, eroding profitability due to inadequate metrology is likely to become an increasingly important issue. As the industry moves down the roadmap into the deep-sub-100 nm domain, eroding CD and overlay error margins shrink into the single-digit range placing enormous pressure on the metrology infrastructure. To meet this challenge, new metrology technology needs to be developed and improvements in the entire dimensional metrology chain will be required. A common misperception is that dimensional metrology during IC manufacturing is limited to off-line CD and overlay tools. However, all precision tools that require a stage are dependant on a means of high-precision real-time displacement measurement, typically performed by a laser interferometer or optical encoder. This includes lithography scanners, mask writers, and metrology tools for CD, overlay and pattern placement. Errors introduced by displacement metrology tools such as interferometers compromise both the quality and yield of patterning and our ability to accurately assess pattern errors. The dimensional metrology infrastructure rests ultimately on the international length standard based on the wavelength of light. This is typically transferred to workpieces by means of an interferometer. While interferometers can have very high precision, their accuracy is compromised by a host of factors, the chief being the influence of the atmosphere. In a well-controlled environment, a laser interferometer can have a repeatability of ~ 10 nm and an accuracy of ~ 100 nm. In vacuum, interferometer accuracy is limited to ~ 2 nm due to a number of optical and electronic non-linearities. Even at the 65 nm node, these errors consume an unacceptable portion of the CD and overlay budgets. In this presentation, the limitations of laser interferometers will be discussed followed by results of recent progress in our laboratory to develop high-accuracy optical encoder gratings which have the potential for much higher accuracy than laser interferometers.

10:30 AM C3.5

The Chemistry and Atmospheric of Inorganic Salt Formation on DUV Exposure Tool Lenses and Reticles.

Uzodinma Okoroanyanwu¹, Andre Pooch¹, Uwe Knappe¹, Torsten Fahr¹, Astrid Gettel¹ and Wolfram Grundke¹; ¹Strategic Lithography, Advanced Micro Devices, Sunnyvale, California; ²Lithography, Advanced Micro Devices, Dresden, Saxon, Germany; ³Lithography, Advanced Micro Devices, Dresden, Saxon, Germany; ⁴Materials Analysis, Advanced Micro Devices, Dresden, Saxon, Germany; ⁵Materials Analysis, Advanced Micro Devices, Dresden, Saxon, Germany; ⁶Lithography, Advanced Micro Devices, Dresden, Saxon, Germany.

Accumulating experimental evidence describe the formation of inorganic crystals that cause haze defects on 193nm and 248nm exposure reticles [1,2] and lenses. These haze defects have been termed progressive defects because they cause catastrophic defect growth over the course of production usage of the lens and reticle in the fab. Although these progressive defects have been observed at almost all lithographic wavelengths, the problem is especially severe in 193 nm lithography, because of the highly energetic (6.4 eV) photons and the concurrent transition to 300 nm wafers, which require photomasks and lenses to endure more prolonged exposure compared to 200 nm wafers. Raman spectroscopic compositional analyses of these crystals have shown them to be made of mostly ammonium sulfate ((NH₄)₂SO₄). Despite a few papers that have been written on the nature and origin of these defects [1,2], there is still no consensus on the mechanism of their formation. While these papers addressed aspects of some possible reaction pathways of the mechanism, there is still no comprehensive treatment that embodies the true atmospheric processes that mediate the chemical transformations that lead to these crystals. This paper is our attempt to remedy this situation. In this paper, we establish that physical and chemical processes in the exposure chamber of DUV steppers and scanners are responsible for the formation of inorganic salts from precursor gases - SO₂, NO_x - contained in the purge air of the tool. Further, we present how these precursor gases, buoyed by atmospheric processes are oxidized to H₂SO₄ and HNO₃, respectively, by oxidants (OH-, O₃, H₂O₂) generated from O₂ and H₂O by the exposure tool laser. Once formed, the H₂SO₄ and HNO₃ react with NH₃ to form the corresponding salts - (NH₄)₂SO₄ and ammonium nitrate (NH₄NO₃), respectively. It should also be mentioned that there are many chemical pathways through which SO₂ and NO_x in the purge air of the exposure tool can be oxidized into sulfates and nitrates, including homogenous processes that take place in the gas phase and

in liquid droplets or heterogeneous processes that take place on the surface of particles or droplets. References [1] B. Grenon, K. Bhattacharyya, W. Volk, A. Pooch, "Reticle surface contaminants and their relationship to subpellicle particle formation", 23rd Annual BACUS Symposium on Photomask Technology, Proceedings of SPIE, Vol. 5256, September 2003. [2] E. Johnstone, L. Dieu, C. Chovino, J. Reyes, D. Hong, P. Krishnan, D. Coburn,, C. Capella, "193nm Haze Contamination: A Close Relationship between Mask and its Environment", 23rd Annual BACUS Symposium on Photomask Technology, Proceedings of SPIE, Vol. 5256, September 2003.

10:45 AM C3.6

Dynamics of an Electrostatic Pin-Chuck and the Mask Response in the EUVL Exposure Tool. Gerald Dicks, Andrew Mikkelsen, Roxann Engelstad and Edward Lovell; University of Wisconsin, Madison, Wisconsin.

The mask used in Extreme Ultraviolet Lithography (EUVL) is expected to experience 5 to 6 g acceleration and achieve speeds of 400 to 500 mm per second while mounted in the exposure tool. Therefore, it is critical that the mounting technique employed to hold the mask in position prevents the mask from slipping under these conditions. Since EUVL takes place in a vacuum, an electrostatic mount has been proposed. A mount of this type relies on adequate pressure between the mask and chuck as well as a sufficient amount of friction to prevent slipping during lateral motion. One such design, the electrostatic pin-chuck, consists of a bed of pins to support the mask in order to minimize the likelihood of particulates becoming lodged between the mask and chuck that would adversely distort the mask. To ensure the success of a mount of this type, three-dimensional finite element (FE) models have been created to predict the conditions necessary to prevent slipping of the mask while mounted in the exposure tool. The mask consists of a standard ultra-low expansion (ULE) substrate, measuring 152.4 mm x 152.4 mm x 6.35 mm, with a 280 nm thick reflective multilayer deposited on the top surface. A typical acceleration cycle is sinusoidal with an amplitude of 6 g and a period of 25 ms. The FE results for a rigid mask on a solid, rigid chuck indicate that the in-plane displacements of the mask relative to the chuck is a function of the coefficient of friction. Results also clearly show, for this case, that inertia forces experienced by the mask exceed the maximum possible friction force and the mask slips relative to the chuck at coefficients of friction of ~ 0.1 and smaller. Theory for this case indicates a minimum coefficient of friction of 0.0825 to prevent slipping of the mask. Thus, the FE results demonstrate the viability of evaluating electrostatic mounts in this way while providing an invaluable tool for perfecting the final design. This paper will include FE results from parametric studies of required interface conditions including contact pressure, friction, pin design (size, spacing, stiffness), mask backside characteristics (nonflatness) and the identification of compatible materials to achieve a viable design.

11:00 AM C3.7

Multilayer X-ray Mirrors for the EUV-lithography Prepared by Ion Beam Sputter Deposition. Bernd Rauschenbach, Eva Schubert, Thomas Hoeche and Horst Neumann; Leibniz-Institut fuer Oberflaechenmodifizierung, D-04318 Leipzig, Germany.

Introduction of new application field such as extreme ultraviolet lithography (EUVL) and x-ray microscopy require a continual improvement in the performance of their optical imaging systems. While 248 and 193 nm optical lithography can be extended to support integrated circuit manufacturing until 100 nm, a next generation lithography technology will be necessary for printing features with size ≤ 50 nm. This requires the application of reflective imaging systems consisting of multilayer stacks working near normal incidence. A primary goal is to maximize the normal incidence reflectance. To achieve optimum performance the multilayer period and layer thickness ration has to be optimised in order to obtain a coherent superposition of lighth waves reflected from each other. On this basis, scaling is expected to support further lithography generations even down to possibly 30 nm. By means of ion beam technologies, layer stacks for reflection optics in the soft x-ray region composed of an alternating arrangement of low- and high-Z materials with individual layer thickness in order of nanometers, can be fabricated on suitable substrates. In the present paper a multi-target process modulus system for the low-energy ion beam sputter thin film deposition in the UHV with the option to deposit Mo/Si-multilayers is used. The process module includes a RF ion source (13.4 MHz) equipped with a focusing two grid system. The multilayer stack consist of a 12 nm Si buffer layer with overcoated by up to 50 periods of 2.7 nm Mo / 4.0 nm Si bilayers deposited on 2 and 6 inch Si(100)substrates at room temperature using Xe or Ar ion assisted sputter deposition. The thickness ratio is chosen to satisfy the Bragg condition for 13.4 nm wavelength at normal incidence. The structure, composition, thermal stability and roughness of individual layers as well as complete stacks, their interface and optical properties are analysed by high-resolution transmission electron microscopy, spectroscopic ellipsometry, atomic

force microscopy, secondary ion mass spectrometry, Cu-K α glancing incidence angle reflectivity and also by x-ray reflectivity measurements between 12.4 and 14.6 nm.

11:15 AM **C3.8**

Dynamic Simulation of Discharge and Laser Produced Plasmas in EUV Lithography Devices. Ahmed Hassanein¹, V. Sizyuk¹, V. Tolkach¹, V. Morozov¹, I. Konkashbaev¹, T. Sizyuk¹ and B. Rice²; ¹Energy Technology Division, Argonne National Laboratory, Argonne, Illinois; ²Components Research Division, Intel Corporation, Hillsboro, Oregon.

Both Laser and Discharge produced plasma are being used as a light source for EUV (extreme ultraviolet) lithography. A key challenge for Discharge Produced Plasma (DPP) devices is achieving sufficient brightness to support the throughput requirements of High-Volume Manufacturing (HVM) lithography exposure tools. One method for improving source brightness is to simulate the source environment in order to optimize the EUV output. An integrated model for the description of hydrodynamics and optical processes in a DPP device has been developed and integrated into the HEIGHTS EUV computer simulation package. Model development consisted of three main tasks: plasma evolution and magnetohydrodynamic (MHD) processes; detailed photon radiation transport, and physics of plasma/electrode interactions in DPP devices. Plasma flows have multidimensional character in pinch systems. Advanced numerical methods for the description of magnetic compression and diffusion in a cylindrical geometry are used in the HEIGHTS package. The package can also study detailed hydrodynamic and radiation processes in various laser produced plasma (LPP) devices as a function of laser energy, wavelength, and dimensions to optimize brightness throughput. For the opacity calculations several models have been developed and implemented. Radiation transport of both continuum and lines is taken into account with detailed spectral profiles in the EUV region. A multi-group approximation of opacities with detail resolution of several thousand strong spectral lines is used. Radiation transport is solved using two different methods, i.e., by direct integration of the transport equation and by 3-D Monte Carlo techniques. Discharges using Xenon and Tin gases are simulated and compared. Response of electrode materials in DPP devices to plasma particles and radiation interactions are also studied. The HEIGHTS package can be used to optimize brightness throughput in both DPP and LPP devices.

SESSION C4: Photoresist Development and Fundamentals

Chairs: Marie Angelopoulos and Christopher Ober
Tuesday Afternoon, November 30, 2004
Republic A (Sheraton)

1:30 PM *C4.1

Additive-Containing Rinses for Image Integrity Control on Advanced Lithographic Patterning. Dario L. Goldfarb¹, Sean D. Burns¹, Ryan L. Burns², Spyridon Skordas³, Colin C. Brodsky², Marie Angelopoulos¹, Erin L. Jablonski⁴, Vivek M. Prabhu⁴, Michael X. Wang⁴, Bryan D. Vogt⁴, Eric K. Lin⁴, Wen-li Wu⁴, Sharadha Sambasivan⁴ and Daniel A. Fischer⁵; ¹T.J. Watson Research Center, IBM Corporation, Yorktown Heights, New York; ²Microelectronics Division, IBM Corporation, East Fishkill, New York; ³School of NanoSciences and NanoEngineering, State University of New York, Albany, New York; ⁴Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ⁵Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

The success of the electronics industry is partially due to meeting the demand for continuously shrinking dimensions that is required to create faster and more densely packed semiconductor devices in a single integrated circuit. With the nearing advent of sub-50 nm lithographic nodes, imaging capabilities are challenged by stringent requirements for materials that can simultaneously provide high spatial resolution, sensitivity, etch selectivity and aspect ratios, together with low absorbance, line edge roughness (LER) and defectivity, among other factors. Given the delicate balance existing between the aforementioned factors, alternative processing methodologies that can address such parameters individually are desirable. In this work, a generalized post-processing method based on the use of additive-containing rinses is proposed as a way to improve the image integrity control of photoresist features. Namely, a reduction on the extent of resist LER, a decrease on the number of resist-originated defects or an increase on the achievable aspect ratios of resist features is possible, depending on the specific chemical nature of the additives incorporated to the rinse, while using a unified rinse dispense method. The mechanisms that justify the observed image integrity improvement on a variety of 193nm resist systems are based on interfacial interactions present between the additive contained in

the rinse and the resist surface. Additive adsorption at the polymeric resist surface and diffusion into the bulk resist can lead to controlled polymer surface plasticization, resulting in a decrease of the high-frequency component of the line edge roughness. Resist defectivity originated from marginally soluble developed resist material can be inhibited when a suitable additive is allowed to adsorb to the resist surface, which leads to the creation of repulsive forces between additive-coated resist surfaces that stabilize the defects in the rinse solution. Increased aspect ratios can be achieved by the modulation of the surface tension of the rinse liquid and the contact angle between the rinse and the resist, inducing an overall decrease of the capillary forces present between patterns during the drying step. The effect of chemical structure and concentration of the additive and contact time with the resist surface are evaluated for a variety of materials that includes ionic and non-ionic short chain molecules and polymers. Analytical techniques are used to monitor the extent of additive adsorption to resist surfaces in-situ (QCM, ellipsometry) and ex-situ (TXRF, NEXAFS) and to characterize the nature of the resist surface (AFM). Finally, the advantage of including an additive in the rinse step instead of using an additive-containing developer is discussed in terms of critical dimension bias and overall image integrity control.

2:00 PM C4.2

Characterization of the Aqueous Base Distribution within Immersed Sub-100 nm Photoresist Thin Films: Dissolution Fundamentals. Vivek M. Prabhu¹, Bryan D. Vogt¹, Erin L. Jablonski¹, Christopher L. Soles¹, Eric K. Lin¹, Wen-li Wu¹, Sushil K. Satija², Dario L. Goldfarb³, Marie Angelopoulos³ and Hiroshi Ito⁴; ¹Polymers Division, NIST, Gaithersburg, Maryland; ²Center for Neutron Research, NIST, Gaithersburg, Maryland; ³TJ Watson Research Center, IBM, Yorktown Heights, New York; ⁴Almaden Research Center, IBM, San Jose, California.

The development step is critical to the fabrication of nanostructures in chemically amplified photoresist technology. With critical dimensions (CD) shrinking to sub-100 nm and the concurrent reduction in exposure radiation wavelength, line-edge roughness (LER) is becoming more important to control. One method is to identify the contributions to LER from the development step, which requires an improved framework. The aqueous base TMAH is typically used to selectively dissolve radiation-exposed photoresist by shifting the chemical equilibrium from the un-ionized to ionized form. New experimental data demonstrate the ionization of the photoresist in aqueous base leads to polyelectrolyte behavior in the model 248 nm material poly(4-hydroxystyrene) and the 157 nm poly(norbornene hexafluoroisopropanol), as demonstrated by small-angle neutron scattering (SANS). This ionization is responsible for both observed thin film swelling and dissolution. The mechanism of dissolution and correlation to the final surface roughness remains a technical challenge. We present a novel methodology of measuring the aqueous base profile and resulting thin film swelling by zero-average contrast immersion neutron reflectivity. This method quantifies the total film swelling, complemented by a quartz crystal microbalance technique, but also provides the first measurement of the aqueous base profile and dependence on pH and polymer thin film composition, within sub-100 nm thin films. These experiments provide new data that can be incorporated into future models for encapsulation and dissolution models.

2:15 PM C4.3

Fundamental Studies of the Dissolution Behavior of Model Photoresist Resins Based on Substituted Polynorbornenes. Clifford L. Henderson¹, Trevor Hoskins¹, Paul J. Roman¹, Larry Seger² and Larry Rhodes²; ¹School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Promerus Electronic Materials, Brecksville, Ohio.

Alicyclic polymer resins, such as those based on substituted polynorbornene (PNB), are one potential material solution for providing photoresist polymers for sub-100nm photolithography. Previously, we have found that one particular form of substituted PNB, namely bis-trifluoromethyl carbinol substituted PNB (HFAPNB), displays an unusual dissolution rate behavior at low to intermediate molecular weights in which the dissolution rate of the polymer increases with increasing polymer molecular weight. This unusual phenomena was attributed to the influence of polymer conformational changes as a function of molecular weight on the extent of interchain ordering and hydrogen bonding in this material. A series of experimental studies on related factors also agree with this hypothesis. A summary of these results for HFAPNB will first be briefly presented. As an extension to this earlier work, the dissolution behavior of other base soluble, substituted PNB materials has been studied. In particular, we have successfully characterized the dissolution rate behavior of trifluorosulfonamide substituted poly(norbornene) or TFSPNB. It was found that in contrast to HFAPNB, TFSPNB polymers do not display any unusual dissolution

rate behavior as a function of molecular weight. In other words, the dissolution rate of these polymers decreases as the polymer molecular weight increases. Their dissolution behavior is consistent with other polymer resins, such as novolac and poly(hydroxystyrene), typically used in photoresist systems. At first glance this result would seem to contradict the earlier findings related to HFAPNB. However, detailed FTIR studies have shown that TFSPNB polymers display a much higher level of interchain hydrogen bonding than HFAPNB polymers, and this hydrogen bonding is not significantly disrupted by conformational effects induced by chain molecular weight. A detailed explanation of these results related to TFSPNB materials will be presented. What evolves from this picture is a general understanding of what is required in order to be able predict what polymers can be successfully inhibited by dissolution rate inhibitors and which materials will display anomalous dissolution behavior as a function of molecular weight. A discussion of the general insights provided by this work on the interplay between polymer structure and dissolution behavior will be provided along with the implications of these results for photoresist formulation. Finally, substituted PNB polymers can display different stereochemical configurations of the base soluble functional groups. We have synthesized stereochemically pure forms of these substituted polymers along with copolymers of the stereochemically pure monomers and characterized their resulting properties. A discussion of the influence of substituent group stereochemistry on the dissolution behavior and other properties of substitute PNB materials will thus also be presented.

2:30 PM C4.4

Photoresist Polymers with Polymer Bound Photoacid

Generators: Fundamental Characterization of Photochemical, Diffusion, and Resolution Behavior. Clifford L. Henderson¹, Cody M. Berger¹, Kenneth E. Gonsalves² and Muthiah Thiyagarajan²;

¹School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Department of Chemistry, University of North Carolina-Charlotte, Charlotte, North Carolina.

As device dimensions continue to diminish below the 100 nm size scale, there is increasing difficulty in delivering photoresist materials with the high sensitivity and resolution required for producing such fine features. Traditional chemically amplified photoresists (CARs) which rely on the use of polymer resins formulated with small molecule photoacid generators (PAGs) will likely be unable to meet the sensitivity, resolution, and line edge roughness demands of these future device generations. Therefore, our work has recently focused on developing chemically amplified photoresists which are based on polymers in which the photoacid generators are bound directly to the polymer backbone. This offers several potential advantages: (1) more uniform PAG distributions and higher PAG loadings can be achieved since the PAG can not phase separate from the polymer resin, (2) the diffusion coefficient of the photoacid can be significantly reduced by binding the PAG to the polymer, and (3) the photochemical reactivity of the PAG may be enhanced by binding the PAG to the polymer which may serve as a chromophore for sensitization. This paper will present results for our most recent work on these polymer-bound PAG CARs. For these CARs, the bulky alicyclic protective group, 2-(4-methoxybutyl)-2-adamantyl was used. This has the effect of improving lithographic performance parameters such as sensitivity, contrast, etch resistance and reducing outgassing during imaging. In addition, to avoid problems like phase separation, non-uniform acid distribution and migration during temperature fluctuations, such as baking processes, PAGs, (phenylmethacrylate)dimethylsulfonium triflate (ionic), N-styrenesulfonyloxy-5-norbornene-2,3-dicarboxyimide (covalent) and N-styrenesulfonyloxy phthalimide (covalent) were incorporated in the polymer main chain. p-Hydroxystyrene was also included to improve adhesion to the substrate. The polymers have been characterized by GPC, NMR, IR, and thermal techniques. The photochemical reactivity of the PAGs in these systems have been characterized using a variety of methods, and a comparison will be made showing the differences between the photochemical rate constants for the polymer bound PAG materials and analogous mixed PAG-polymer systems. It will be shown that in some cases the attachment of the PAG to the polymer can enhance the photochemical reactivity of the PAG while in other cases the binding of the PAG can dramatically lower its reactivity. Additionally, the diffusion coefficient of the polymer-bound PAGs has been characterized and comparisons of this diffusion behavior with analogous mixed polymer-PAG systems will also be made. Finally, results from high resolution patterning and resolution tests using these polymer bound PAG photoresists will be shown and compared to current CAR materials.

2:45 PM C4.5

Fundamental Studies of the Thickness Dependent Behavior of Photoresist Ultrathin Films: An Overview and Update.

Clifford L. Henderson and Lovejeet Singh; School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Fabrication of future nano-scale electronic devices will likely require the use of ultra-thin resist films. It has been observed that film thickness, molecular weight, and substrate interactions can significantly affect the thermophysical properties of polymer thin films such as the glass transition temperature, coefficient of thermal expansion, and most recently the diffusion coefficient of small molecules in polymer ultra-thin films. Changes in such film properties can potentially have an impact on the lithographic performance of polymer thin film photoresists. This paper will serve to: (1) summarize many of our recent results on the fundamental thermophysical and diffusion behavior of model photoresist ultrathin films and (2) discuss our most recent results on the influence of film thickness on a variety of other lithographically important polymer properties. As an extension of this work, we have most recently studied the dissolution rate properties of polymer ultrathin films. Simulation of lithographic processes relies to a great extent on knowledge of the dissolution or development behavior of photoresist thin films. Resist contrast is also known to be strongly affected by the dissolution behavior of the resist matrix polymer. So far, the possibility of film thickness significantly affecting the dissolution behavior of thin photoresist films has generally been ignored. This paper will summarize our work focused on determining the effect of film thickness on the dissolution behavior of a variety of resist polymers including novolac, polyhydroxystyrene (PHOST), and bis-trifluoromethyl carbinol substituted polynorbornene (HFAPNB). It was observed that both poly(hydroxystyrene) (PHOST) and bis-trifluoromethyl carbinol substituted polynorbornene (HFAPNB) exhibit strong surface acceleration behavior as compared to the classic surface inhibition that has been extensively studied in novolac polymers. Most importantly, the dissolution rate of PHOST and HFAPNB thin films was found to depend strongly on the thickness of the polymer film for film thicknesses below a critical thickness value. It was found that a key factor, which may explain this dissolution behavior, which varied in the films as a function of film thickness was the extent of hydrogen bonding of hydroxyl groups in the polymer film. The implications of such anomalous behavior on the formulation and processing of photoresist ultra-thin films will be discussed.

3:30 PM C4.6

NEXAFS characterization of surface phenomena in chemically amplified photoresists.

Erin Jablonski^{1,2}, Daniel Fischer², Sharadha Sambasivan², Eric Lin² and Vivek Prabhu²; ¹Chemical Engineering, Bucknell University, Lewisburg, Pennsylvania; ²NIST, Gaithersburg, Maryland.

Chemically amplified photoresists are sensitive to certain airborne molecular contaminants, notably amines, during post exposure delay, though the actual cause and specific failure mechanism are unknown. To assess the effect of low concentrations of atmospheric species on the performance of chemically amplified photoresists, an environmentally controlled system has been developed that allows fine tuning of processing conditions coupled with immediate surface and bulk chemical characterization using near edge x-ray absorption fine structure spectroscopy (NEXAFS). In order to quantify component segregation and identify surface phenomena that may be responsible for pattern degradation, the surface and bulk chemistry of model photoresists were analyzed using NEXAFS equipped with in situ processing capabilities for exposure, controlled dosing of a model contaminant gas, and heating. It has been found that photo-acid generator segregates to the surface of the photoresist film; as film thickness becomes progressively thinner and the chemistry of the photoresists changes as more fluorinated components are incorporated, the behavior of this PAG-rich, high fluorine content surface layer may introduce additional/unique sensitivity to airborne contaminants and failure mechanisms compared to previous photoresist materials. This technique is therefore valuable to elucidate the influence of atmospheric contaminants in next generation chemically amplified photoresists, particularly with the move toward new chemistries and thinner films, which have been shown to be more environmentally unstable compared to past materials. In addition, use of photoresist blend formulations at the 157 nm node presents a number of materials issues, including polymer/substrate and polymer/air interfacial (surface energy) effects, blend miscibility, and small molecule diffusion in thin films. NEXAFS has been used probe the surface and bulk chemistry of these chemically amplified photoresists to determine possible causes of pattern degradation, including polymer component and small molecule diffusion/segregation to the photoresist surface and interactions between components of the photoresist formulation and developer. We find significant segregation of one blend component to the polymer film surface and discuss implications for the performance of thin film blend photoresists.

3:45 PM C4.7

Molecular Glass Photoresists for Advanced Lithography.

Da Yang, Junyan Dai, Nelson M. Felix, Seung Wook Chang and Christopher K. Ober; Materials Science & Engineering, Cornell University, Ithaca, New York.

To meet the growing demand of fabricating more advanced and powerful semiconductor devices, new resist materials need to be developed to reduce the minimum feature size. Most existing resist materials are based on organic polymers. Although organic polymers possess many beneficial features, i.e., amorphous nature, flexibility, processability, desirable for lithographic applications, there are also shortcomings associated with their polymer nature. One example is the resolution limitation resulting in line edge roughness (LER), due to the large molecular size and size distribution of the polymers. Although low molecular-weight resist materials are expected to provide the needed breakthrough for reducing the edge and surface roughness of patterns, they generally tend to crystallize readily, and hence lack the ability to form uniform amorphous films. Our research has focused on the creation and lithographic evaluation of low molecular-weight organic resist materials that readily form stable amorphous glasses above room temperature, which we refer to as "molecular glasses", as well as on establishing the guidelines for the design of amorphous molecular materials. We have prepared novel families of molecular glass materials that function as both positive and negative resists capable of producing features as small as 60 nm line/space patterns on exposure to a 100 keV electron beam. Molecular glass resists also showed much less surface roughness and line edge roughness, as well as good etch resistance comparing to polymeric resists.

4:00 PM C4.8

A Study on Surface and Pattern Roughness of Low Molecular Weight Polyphenols. Taku Hirayama¹, Daiju Shiono¹, Shogo Matsumaru¹, Toshiyuki Ogata¹, Hideo Hada¹, Junichi Onodera¹, Tadashi Arai², Toshio Sakamizu², Atsuko Yamaguchi², Hiroshi Shirashi², Hiroshi Fukuda² and Mitsuru Ueda³; ¹Research and Development Department, Tokyo Ohka Kogyo Co., Ltd., Samukawa-machi, Koza-gun, Kanagawa-ken, Japan; ²ULSI Research Department, Hitachi, Ltd., Center Research Laboratory, Kokubunji-shi, Tokyo, Japan; ³Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo, Japan.

We have investigated the possibility of amorphous low molecular weight polyphenols as a chemically amplified positive-tone electron-beam (EB) resist. Two low molecular weight polyphenols, 4,4'-methylenebis[2-[di(2-methyl-4-hydroxy-5-cyclohexylphenyl)]methyl]phenol (3M6C-MBSA), and 4,4'-methylenebis[2-[di(4-hydroxy-2,5-dimethyl-phenyl)]methyl]phenol (25X-MBSA) as a base matrix, and poly(p-hydroxystyrene) (PHS) with a weight average molecular weight of 8400 as a reference were selected. Those phenol groups were protected by 1-ethoxyethyl groups to control the dissolution rate of these materials in 0.26 N tetramethylammonium hydroxide (TMAH) aq. developer. Etching rates under CF₄/CHF₃/He mixed gas process, dissolution rates with the developer, sensitivities with EB exposure, resolution and surface roughness were evaluated. The resist based on 3M6C-MBSA showed the excellent pattern profile and 60 nm lines and spaces (lines/spaces=1/1) resolution. And, even 50 nm lines and spaces pattern was partially re-solved. In addition, as compared with PHS, smaller surface roughness of 3M6C-MBSA films was observed by AFM measurement.

4:15 PM C4.9

Methods for Enhancing the Sensitivity of Hydrogen Silsesquioxane for sub-100 nm Electron Beam Lithography. Clifford L. Henderson and Augustin Jeyakumar; School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Hydrogen-silsesquioxane (HSQ) is a negative tone electron beam resist that has received significant interest in high resolution lithography and has been recently demonstrated as a viable nanoimprinting template material. Upon electron beam irradiation, it is believed that the silicon hydride (Si-H) bonds are scissioned to form a silanol (Si-OH) in the presence of absorbed moisture within the film. The unstable silanol further condenses to form siloxane (Si-O-Si) bonds which render the matrix insoluble in a moderate base. However, one of the major drawbacks with HSQ has been the high electron beam dose required to cause crosslinking and network formation. For a 100nm thin film exposed at 100keV, an imaging dose of approximately 1500 $\mu\text{C}/\text{cm}^2$ is typically required to print high resolution patterns. However, Harkness and coworkers demonstrated that the optical sensitivity of HSQ could be substantially enhanced using photobase generators as sensitizers. They attributed this sensitivity enhancement to based catalyzed conversion of the silicon hydride group to the silanol, thus lowering the dose requirement for optical exposure. In this study, the additions of both a photodecomposable base and a photobase generator (PBG) as sensitizers were investigated in terms of their ability to enhance the electron beam sensitivity of HSQ. It was found that the photobase generators that work for optical

exposure provide a slight, but substantially less impressive, improvement in HSQ sensitivity in the case of electron beam patterning. In the case of the photodecomposable base, triphenylsulfonium hydroxide (TPS-OH) was used in an attempt to produce a positive tone version of HSQ in which exposure would decompose the base catalyst that would subsequently promote network formation in unexposed regions. It was found that the TPS-OH and HSQ mixtures did not function in a positive tone manner as might be hoped, but it was found that TPS-OH could be used to both enhance the storage stability of HSQ solutions and the sensitivity of HSQ in a negative tone process. The effects of different additive loadings, post-apply bake temperatures and time, and post-exposure bake temperatures and times on the sensitivity and contrast of HSQ-sensitizer mixtures have been studied systematically. It was found that in all cases, significantly elevated PEB temperatures are required to realize any significant sensitivity enhancements with these additives. PAB conditions were found to have a minimal effect. High resolution patterning using a 100 keV electron beam direct write system has been used to characterize the resolution of HSQ-sensitizer materials and these results will be compared with those of pure HSQ. A discussion of these studies, the results, and the implications of this work for formulation of improved HSQ-based imaging materials will be presented. Additionally, some discussion of alternative molecular architectures that can be investigated will also be discussed.

4:30 PM C4.10

Nanopatterning of Chemical Vapor Deposited Thin Films Using Electron-beam Lithography. Yu Mao¹, Nelson M. Felix², Chris K. Ober² and Karen K. Gleason¹; ¹MIT, Cambridge, Massachusetts; ²Cornell University, Ithaca, New York.

Chemical vapor deposition (CVD) of resist thin films is a dry processing alternative to the conventional spin casting of resists. Elimination of wet chemistry will reduce the environmental impact of lithography and provide more flexibility for integration with other microfabrication processes. However, the sensitivity and resolution of plasma CVD resists are limited due to the crosslinked structure in the deposited films. This paper presents studies of negative-tone and positive-tone nanopatterning in thin films deposited using a unique low-temperature initiated CVD process. Monomers and initiators are fed into a vacuum chamber with a filament resistively heated up, then the polymeric thin films are synthesized in situ and deposited directly on the substrate. The irradiation-sensitive chemical functionalities were retained in this novel process, and a linear polymeric structure was achieved. By controlling film composition and molecular weight, the electron-beam sensitivity of the CVD films can be controlled in the range of 20-50 $\mu\text{C}/\text{cm}^2$. Both negative-tone and positive-tone 80 nm line patterns are achieved to date; further process optimization is expected to resolve finer features. These CVD films exhibit excellent smoothness with root-mean-square (rms) roughness 0.3 nm. This paper also discusses the dependence of film composition, film molecular weight and rms roughness on CVD process conditions.

SESSION C5: Poster Session
Chairs: Rod Kunz and Christopher Ober
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

C5.1

Charged Particle-Surface Interactions in EUV Lithography Collector Mirrors. J.P. Allain¹, Ahmed Hassanein¹, Martin de Jesus Nieto¹, V. Titov¹, C. Chrobak², D. Rokusek³, M.M.C. Allain³, B. Heuser³ and B. Rice⁴; ¹Energy Technology Division, Argonne National Laboratory, Argonne, Illinois; ²Nuclear Engineering and Engineering Physics, University of Wisconsin, Madison, Wisconsin; ³Nuclear, Plasma and Radiological Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ⁴Components Research Division, Intel Corporation, Hillsboro, Oregon.

In extreme ultraviolet lithography (EUVL) environments particle/surface interactions occur for both EUV plasma source components and collector optical elements. Both laser produced plasma (LPP) and gas discharge produced plasma (GDPP) configurations face serious issues of components lifetime and performance under particle bombardment. In LPP, nozzle material can be eroded and analogously in GDPP devices, electrode material is eroded. For both configurations debris material, fast ions and neutrals, and condensable alternate EUV radiator fuels (Li, Sn) can irradiate collector optical surfaces. A critical challenge facing EUVL development is both electrode (in the case of GDPP) and optical component lifetime (in both LPP and GDPP). In addition to: impinging debris, fast ions and neutrals, and condensable EUV fuels (Li, Sn); collector mirrors are exposed to impurities (H,C,O,N), off-band radiation and highly-charged ions leading to their

degradation and consequently limiting 13.5 nm light reflection intensity. The IMPACT (Interaction of Materials with charged Particles and Components Testing) experiment at Argonne studies radiation-induced and thermodynamic mechanisms that influence the behavior of optical mirror surfaces. In GDPP devices grazing incidence mirrors (GIM) are used, while in LPP devices multi-layer mirrors (MLM) for near-normal light incidence are used. Irradiation conditions include: incident particle energy (50 eV - 5 keV), angle-of-incidence (near-normal to oblique), incident flux (10^{11} - 10^{15} ions/cm²/s), and surface temperature (room temp. and up to 400 C). Results of optical component interaction with singly-charged inert gases (Xe) and alternate radiators (Li, Sn) are presented for GIM (Ru, Pd) and multi-layer mirrors (Mo/Si). Critical issues under study include: physical sputtering thresholds and energy dependence, radiation induced segregation of implanted EUV radiator fuel, collisional mixing, amorphization, surface roughness evolution and effect of ion irradiation on EUV reflectivity mirror performance. Measurements conducted include: in-situ quartz crystal microbalance, in-situ surface analysis: auger spectroscopy and ion scattering spectroscopy, X-ray reflectivity, X-ray diffraction and atomic force microscopy.

C5.2

Lens Contamination by Photoresist during Immersion Lithography. Gregory Nellis¹, Alex Wei¹, Mohamed El-Morsi¹ and Chris van Peski²; ¹University of Wisconsin, Madison, Wisconsin; ²International SEMATECH, Austin, Texas.

The premise behind immersion lithography is to increase the index of refraction of the gap between the lens and wafer through the insertion of a high-index liquid in place of the low-index air that currently fills the space. The photoresist contains some components that are soluble in the immersion fluid; this material will therefore be released as the wafer moves under the lens. Depending on the flow conditions and geometry, it is possible that some of these contaminants will diffuse or convect across the lens-wafer gap and contaminate the lens surface. The amount of soluble material in resist is small (on the order of milligrams per cm²) and under most flow conditions only a fraction of this material can reach the lens before it is swept out of the gap. However, the anticipated life of an immersion tool is very long and therefore even a very gradual buildup of contamination can adversely affect the tools maintenance requirements and useful life. This paper describes several diffusion models that are used to predict the concentration distribution for contaminants throughout the lens-wafer gap under scanning conditions that are anticipated for immersion lithography. Finite-difference models are used to calculate the steady-state concentration distribution in the case of fully developed flow in a gap where the pressure gradient driving the flow and the wafer motion are in the same direction, referred to as aligned flow conditions. The concentration distribution is subsequently used to predict the rate at which contamination will reach the lens. It is shown that a negligible amount of contamination reaches the lens under these conditions provided there is any significant flow of immersion fluid. Detailed computational fluid dynamics (CFD) models have been developed to evaluate the more complex flow patterns associated with the case where the pressure gradient driving the flow and the wafer motion are in opposite directions, referred to as the opposed case. The rate of contamination in this configuration is shown to be significantly larger than in the aligned case. Finally, the more complex, 3D flow patterns in the region adjacent to a vertical dispense port are investigated using CFD models. In this region, recirculating velocity distributions may form which will transport contamination from the wafer to the lens surface by convection as well as diffusion. The result is a much higher rate of lens contamination which may be an issue for the implementation of immersion lithography.

C5.3

Dynamics of Droplet Coalescence during Imprint Lithography. Scott Schuetter, Gerald Dicks, Gregory Nellis and Roxann Engelstad; University of Wisconsin, Madison, Wisconsin.

In Step-and-Flash Imprint Lithography, features are transferred from a template by lowering it onto a low-viscosity, photocurable, monomer solution that conforms to the template surface and is subsequently cured. Currently, a single, large droplet is dispensed in the center of the template and the subsequent imprinting process causes the droplet to cover the entire active area. This process results in large pressure forces on the template due to viscous resistance to the flow that must occur in a small gap and over a large distance; from the center to the edge of the template. Low template velocities are utilized to control these viscous pressures, resulting in long process times and low throughput. In order to overcome this limitation, drop-on-demand technology has been developed in which many, smaller volume droplets are dispensed in a regular pattern over the entire active area; the pattern density of the dispensed droplets may be adjusted based on the local pattern density on the template. Many small droplets can be imprinted with a much larger template velocity than a single

droplet. However, the fluid dynamics that governs the response of these droplets is more complicated than for the single droplet case. Initially, the smaller droplets behave as isolated, axisymmetric volumes that increase in radial extent as the imprint progresses in time. Eventually, adjacent droplets come into contact causing the process to enter a complex regime associated with droplet coalescing. Eventually, the droplets have completely coalesced and therefore the system again behaves as one large droplet. During the non-coalesced regime, the fluid dynamic behavior of the imprint process is well understood and governed by the axisymmetric Reynolds equation which has an analytical solution in the limit of a rigid, flat plate. The Reynolds equation is modified based on the physics of the coalescing phenomena in order to remain applicable throughout the imprint process. The modification parameters are based on computational fluid dynamics simulations of coalescing droplets using the volume-of-fluid technique for modeling the free surface. The result is a convenient, analytical solution for the pressure loading as a function of local (over the unit cell occupied by a single droplet) gap height and its time rate of change. The pressure loading expressed in this manner can be applied as the loading for a finite-element structural model of the template and used to predict the out-of-plane and in-plane distortions induced in the template during the imprint process. The model includes the coupled fluid-structure interaction in that global template distortions can affect the applied pressures. The model can be used to study the effect of pattern density variations, template mounting conditions, and imprint process parameters. This paper presents the details of the fluid and structural modeling and discusses their impact on overall process throughput.

C5.4

New Approaches to Nanofabrication by Edge Lithography. Qiaobing Xu, Byron D. Gates and George M. Whitesides; Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

There are many ways to grow thin films with well-controlled thicknesses between 1 and 50 nm over large areas of surface. We developed two techniques to take advantage of this capability to fabricate nanostructures by converting these films - which are thin along the z axis - into structures that are thin along the x axis. In first approach, we developed a procedure to fabricate planar structures comprising nanoscale metallic features embedded in a polymer. These structures are prepared by sectioning a thin metallic film - embedded in a polymer matrix - in a plane perpendicular to the metallic film using the glass knife of a microtome. Sectioning at temperatures below -120 centigrade minimized delamination between the epoxy and metal film, and improved the roughness of the cross-section (~ 10 nm). Using this approach, we fabricated arrays of 50-nm wide, 2- μ m long, gold nanowires; these wires can be addressed electrically from the opposite edge of the encapsulating matrix. The exposed edges are further used to electrodeposit gold nanowires. Ordered arrays of nanoscale edges have also been patterned over large areas ($> \text{cm}^2$) using a method to tip a periodic array of posts - each capped with a metal film - onto one side. Arrays of epoxy pillars (or "microdominos") patterned by conventional photolithography were fractured from the supporting substrate under a horizontally applied shear force. Shearing palladium-capped microdominos generated regular arrays of features with nanometer-scale lateral dimensions in-plane. Transferring these microdominos onto a film of conductive polymer established an electrical connection to each of the arrayed edges. This array of narrow electrodes could be used to print, in parallel, multiple regions of charge in a film of poly(methyl methacrylate).

C5.5

Metal Nanotube Membranes with Sub-100 nm Apertures and their Lithographic Applications. Woo Lee¹, Hong Jin Fan¹, Sung-Kyun Lee¹, Stefan Richter¹, Sven Matthias¹, Wulf Wulfhekel¹, Margit Zacharias¹, Dietrich Hesse¹, Juergen Kirschner¹, Eric Moyer², Margit Hanbuecken², Kornelius Nielsch¹ and Ulrich Goesele¹; ¹Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany; ²CRM-CNRS, Campus de Luminy, case 913, 13288 Marseille Cedex, France.

We report on the fabrication of hierarchically organized arrays of metal nanotubes, which can be used as shadow masks for generating spatially well-resolved 2-D periodic arrays of various nanostructures via sputter deposition, reactive ion-beam etching (RIE), and plasmonic lithography. The metal membranes are formed by a replication technique based on electrochemical deposition of anodic aluminum oxide (AAO) membranes or silicon substrates with lithographically generated etch pits. By controlling the pore diameter of the AAO templates, we could fabricate well-defined and perfectly ordered metal nanotube membranes on a cm²-scale with aperture sizes ranging from 80 to 300 nm. On the other hand, control over the shape and two-dimensional (2-D) arrangement of metal nanotubes could be achieved by using patterned silicon substrates as a master. The nanotube membranes have been successfully used as shadow

masks in sputter deposition of metals and pulsed laser deposition (PLD) of ferroelectric materials to generate 2D-arrays of nanodots. In comparison with conventional photoresist patterning, the metal masks are very suitable for lift-off processes, where high temperatures are required for the substrate during deposition or for nanopatterning within ultra-high vacuum systems. Furthermore, reactive ion-beam etching (RIE) has been employed for the transfer of the membrane pattern to SiC substrates. The growth of 2-D perfect hexagonal arrays of ZnO nanorods on large scale has also been demonstrated, combining the vapor-liquid-solid (VLS) growth process and the present mask technique to define the location of catalytic Au nanodots. The metal nanotube membranes exhibited exceptional optical transmission properties depending on the tube diameter. In this presentation, optical properties of the metal nanotube membranes having sub-wavelength scale apertures will also be discussed.

C5.6

A Novel Quantum-Mechanically Corrected Variational Principle for Modeling Intrinsic Fluctuations in Decanometer Devices due to Gate Line Edge Roughness (LER). Norman Gunther¹, Iliya Petic^{1,2}, Emad Hamadeh^{1,3}, Darrell Niemann¹ and Mahmud Rahman¹; ¹Electron Devices Laboratory, Santa Clara University, Santa Clara, California; ²Silvaco International, Santa Clara, California; ³Applied Micro Circuits Corporation, Sunnyvale, California.

Random fluctuations in fabrication process outcomes such as gate LER give rise to corresponding fluctuations in device characteristics. These fluctuations are intra-die and inherent to the process. As such, they represent fundamental limitations to the die-level uniformity of the properties of otherwise identical devices. Appropriate LER modeling will help understand the effects of these critical dimension fluctuations on device characteristics. Although for devices of channel length greater than 100 nm, the effects of random fluctuations tend to be negligible, they become significant for channel length less than 50 nm. Since we are rapidly approaching technology nodes required by ITRS where these issues are critical, there is need to improve our understanding of the mechanisms which induce them. In particular, for MOS devices of this scale the fringe electric field at the edges of the gate, and the quantum-mechanical effect of charge confinement near the interface play dominant roles in determining the properties of the device and fluctuations in them. It is important that process engineers are apprised of approaching technology nodes for which current engineered materials and processes are inadequate. Presently, TCAD numerical simulation is the only tool available for investigating the complex interaction of these issues. In this work, we employ our novel 3D quantum mechanically corrected variational principle (VQM) based on minimization of the electrostatic energy (see Journal of Applied Physics, Vol. 95, No. 4, pp. 2063-2073) which offers a mathematically distinct path to address the problem. Based on the device level consequences of gate LER as modeled by our approach, it will be possible to specify LER control design rules for aggressively scaled MOS devices at approaching technology nodes. Gate LER significantly increases the perimeter of the gate while having minimal effect on the area. This increase in the perimeter can be expressed in terms of a deterministic part plus its device-to-device random variance, and can be quantified using the statistical properties of the LER. Empirical LER wavelength data have been found to be well represented by a lognormal distribution in frequency. These data can be incorporated in our VQM model yielding expressions for the variance of capacitance, threshold voltage, etc., due to LER as a function of device gate dimension, oxide thickness, and doping. Our results can be used to quantify process with successful integration of LER effects.

C5.7 TRANSFERRED TO C1.7

C5.8

Particle Minimized EUV-mask Blank Deposition by Ion Beam Sputtering. Bernd Rauschenbach¹, Horst Neumann¹, Jens Dienelt¹, Frank Scholze¹, Eva Schubert¹, Matthias Nestler² and Mirko Schulze³; ¹Leibniz-Institut fuer Oberflaechenmodifizierung, D-04318 Leipzig, Germany; ²Roth & Rau AG, D-09337 Hohenstein-Ernstthal, Germany; ³AIS Automation GmbH, D-01237 Dresden, Germany.

The development of sophisticated process technology for the fabrication of miniaturized high-quality microelectronic components is a demand of the future IC manufacturing. Lithography with small exposure wavelength at 13.4 nm (EUV spectral region) will be a key technology therefore. Mask blanks for the lithography in the soft x-ray region are based on reflection optics consisting of a low index / high index multilayer stack with special demands concerning thickness homogeneity and particle impurities. A new ion beam sputter deposition tool is developed which allows Mo/Si multilayer fabrication with a thickness homogeneity of less than 0.1 % over an area of 6 inch square and a minimization of particle generation during handling. The deposition equipment consists a segmented linear electron cyclotron

resonance (ECR) ion beam source (600 mm beam width), a substrate holder with translation movement and a turnable target holder. The 30 segments of the ion beam source can be independently controlled and therefore the ion current density profile individually adjusted. The design of the ion source grids is optimized for a low ion beam divergence. Both, the application of the linear sputter ion source a a substrate translation during deposition are necessary to obtain the demand thickness homogeneity. Additionally, the thickness of the Mo/Si-layers will be controlled by in-situ ellipsometry measurements with an accuracy of better than 0.06 nm. Furthermore the ellipsometric parameters provide inabout the stack sequence. The particle generation during the deposition process ist generally a great problem. Therefore the number of direct contact events with the mask blank should be minimized as well as low particle generating material combinations and vacuum components should be found. In the present concept a vertical handling of the mask blank without clamping and chucking is realized. For this a very stable magnetically coupled rodless cylinder is used. This component is specified with a low particle generation of less than 0.1 particle per cycle for particle sizes greater than 100 nm.

C5.9

Characterization of Line Edge Roughness of Sub-100nm Patterned Photoresist Based on Acryl Polymers.

Toshiyuki Ogata, Taku Hirayama, Shogo Matsumaru, Daiju Shiono and Hideo Hada; Research & Development, Tokyo Ohka Kogyo Co., Ltd., Koza-Gun, Kanagawa-ken, Japan.

The control of line edge roughness (LER) in patterned resist lines is a major challenging topic in manufacturing of semiconductors. We have reported effect of protecting group of polymer materials on lithographic performance for the designing of chemical amplification positive-tone resist system. The results suggested that alkoxymethyl-protecting group should be effective for further controlling LER. Preparing different copolymer Poly (2-adamantylloxymethylmethacrylate-co- γ -butyrolactonemethacrylate: AdOMMA-co-GBLMA) and Poly (2-methyl-2-adamantylmethacrylate-co- γ -butyrolactonemethacrylate: MAdMA-co-GBLMA), we have evaluated LER of 120nm resist lines using 193nm lithography. In the comparison of AdOMMA-co-GBLMA and MAdMA-co-GBLMA, the observed LER were 5.6 nm and 7.6 nm, respectively. One of the modified AdOMMA polymers controlled composition ratio of AdOMMA, less than 5nm LER was observed.

C5.10

Resist Materials for EUV Lithography. Kenneth E. Gonsalves¹, Jae H. Choi¹, Muthiah Thiyagarajan¹ and Paul Zimmerman²; ¹Chemistry, University of North Carolina@Charlotte, Charlotte, North Carolina; ²International SEMATECH, Austin, Texas.

Extreme UV lithography (EUVL) is a promising candidate for sub-100-nm pattern generation down to the 32 nm node. Chemically amplified resist materials for EUVL should have high sensitivity, contrast, etch resistance, low line edge roughness, low outgassing, and also compatibility with a conventional developer. EUVL requires a vacuum environment for exposing the resist, hence outgassing should be reduced drastically or preferably eliminated. We have synthesized polymers containing the bulky adamantly protecting group to improve sensitivity, resolution, and etch resistance. Poly[4-hydroxystyrene-co-2-(4-methoxybutyl)-2adamantyl methacrylate] resist systems show 60 nm line positive patterns (pitch 180 nm) at a dose of 11.2 mJ/cm² and a 33 nm line/space negative pattern at a higher dose. We have also incorporated a photoacid generator (ionic and covalent) in the main chain of the polymer to enhance sensitivity and contrast. We were able to image PAG bound poly(hydroxystyrene-co-ethyladamantylmethacrylate-co-PAG) to 70 nm line/space patterns using EUV exposure. It should be mentioned that base was incorporated in all the above formulations to control acid diffusion. * Corresponding Author, E-mail : kegonsal@email.uncc.edu

C5.11

Generating Production-Worthy Sub-35nm Gates with Amorphous Carbon. Hartmut Ruelke², Rolf Stephan², Karla Romero², Martin Mazur², Gunther Grasshoff², Katja Huy², Wendy Yeh¹, Sudha Rathi¹, Frank Koestner³, Wolfgang Senninger³, Meggy Gotuaco¹ and Susan Weiher-Telford³; ¹Applied Materials, Santa Clara, California; ²Advanced Micro Devices, AMD Saxony LLC&Co KG, Dresden, Germany; ³Applied Materials Europe, Dresden, Germany.

A new approach has been developed to enable sub-40nm gates. Rather than using photoresist and a silicon based dielectric hardmask as the patterning layer, this gate patterning scheme uses an amorphous carbon and dielectric hardmask. Sub-40nm gate lengths have been consistently manufactured with this scheme, while 30nm gate length has also been demonstrated. Several benefits are observed with this

approach, including low consumption of resist, simple integration by eliminating wet etch removal of the hardmask, and potentially, faster chips, resulting from the ability to achieve a smaller gate length. The dual layer hardmask comprises an amorphous carbon film beneath a dielectric cap. The a:C and capping layer are deposited by a PECVD process on a production proven mainframe. The amorphous carbon film works as an anti-reflective coating that absorbs light to minimize reflection. The anti-reflectivity properties is further enhanced by the capping layer, which can be made of a dielectric anti-reflective coating with adjustable thickness and optical film properties to minimize reflectivity for optimal lithography results. Superior reflectivity control and CD swing obtained on this dual layer will be presented. An advanced 193nm lithography processing is used in combination with this film stack. The a:C film exhibits good interface behaviour to various underlayer films including poly-silicon, TEOS and silane oxide, silicon, and nitride layers allowing it to work as a hardmask for various materials. It has good etch selectivity to Si-oxide, nitride and poly-silicon. The PE-CVD deposition process for the a:C and cap layers has proven to have good repeatability for thickness and optical properties, low non-uniformity and good defect performance in a high volume production environment. The defect performance is especially crucial to the implementation of the amorphous carbon film in manufacturing. In-film defects are consistently low at single digit @ > 0.12 μm . Combining the 193nm lithography with a poly gate etch trim integration scheme, the paper will demonstrate how minimal resist budget is needed to generate 30nm using the amorphous carbon dual layer hardmask approach. 30nm gate SEMs showing straight profiles and no broken or fallen lines over topography areas will be presented. This integration scheme for gate etch was proven reliable for manufacturing as it produces consistently low within die and low within wafer CD variation after gate etch. The wafer to wafer CD variation with amorphous carbon is comparable to that achieved with the conventional approach. Post etch defects are shown to be equivalent to that of traditional approaches, and yield is comparable or better than traditional processes.

C5.12

Nanolithography of SiO₂/Si(111) using UHV-STM.

Hyungjin Bang¹, Yasuyuki Kawamura², Etsuko Hosoda², Chisa

Yoshida², Yuka Ito¹, Takahiro Maruyama^{1,2} and Shigeo Naritsuka^{1,2}; ¹21st Century COE program, Meijo University, Nagoya, Aichi, Japan; ²Department of Materials Science and Engineering, Meijo University, Nagoya, Aichi, Japan.

For novel device applications, growth of carbon nanotube (CNT) on desired place with desired structure (chirality) is highly required. Various methods such as standard lithography, soft lithography, and self-assembly are being applied to control the arrangement of CNT with the resolution of micrometer order. However, to clarify the growth mechanism and to control the chirality of CNT, it is necessary to minimize the size of patterning catalysts to the scale of an individual CNT size, which is normally scaled 1 tens of nanometer orders. We report nanolithography on SiO₂/Si substrate using ultra high vacuum scanning tunneling microscopy (UHV-STM) for the purpose of nano-scale controlling of CNT. 1 \times 7 \times 0.3 mm³ size-cut n-type Si (111) substrate was prepared. The conventional degreasing procedure by ultrasonic cleaning was carried out using acetone, methanol, and deionized water in sequence. Then, the substrate was introduced into UHV-STM system (JEOL JSPM-4500). After clear removal of the surface native oxide by flashing at 1200 °C for 15 seconds was undertaken, a thin oxidation layer was formed by heating the substrate at 700 °C for 10 minutes, in an atmosphere of oxygen with the pressure of 5 \times 10⁻³Pa. For the lithography condition, between 80 150eV of bias voltage and 2.5 10nA of tunneling current was used, and surface post-observation was performed with bias voltage and tunneling current with range of 2.0 4.3eV and 0.05 0.3nA, respectively. For both the lithography and the observation, W wire made by electrochemical etching was applied. A nano-size pin-hole was successfully patterned on thermally formed Si oxide on Si (111) substrate. The pin-hole sizes were controlled by regulating the bias voltage and the dose of tunneling current. Within the pin-holes, Si 7 \times 7 reconstruction indicating the clear removal of oxide layers was observed. The pin-hole size's dependence upon detailed lithography conditions will be discussed. Selective patterning of Fe catalyst on this substrate will be carried out and discussed as well.

C5.13

Nano-Lithography on Surface Oxide of GaAs using

UHV-STM. Takahiro Maruyama^{1,2}, Hideaki Uemura¹, Yasuyuki Kawamura², Yuka Ito¹, Yo Yamamoto¹, Hyungjin Bang¹ and Shigeo Naritsuka^{1,2}; ¹21th COE Program "Nano Factory", Meijo University, Nagoya, Japan; ²Department of Materials Science and Engineering, Meijo University, Nagoya, Japan.

The patterning of small features on surface of semiconductor is essential technique for improvement of various electronic device performance, such as VLSI and FET. So far, various techniques have

been attempted for achievement of sub-micron lithography and linewidth of 100nm-scale has been attained by photolithographic technique. However, fabrication of more fine structure will be necessary for realizing novel functional nanometer-scale devices. Electron beam lithography boasts higher resolution than optical technique, but atomic-scale patterning is difficult to achieve by this technique. One of strong candidates for fabrication of nano-scale lithography is SPM technique. Especially, scanning tunneling microscopy (STM) lithography is a powerful tool, since it has potential ability to achieve atomic-scale lithography. In this study, we have attempted to perform STM lithography on surface oxide on GaAs(100) and successfully obtained lithography area of less than 25 \times 25 square nanometers. After chemical etching with solution of NH₄OH:H₂O₂:H₂O=4:1:20, GaAs(100) sample was introduced into UHV-STM chamber. Following pre-thermal treatment at 250°C for 12 hours, lithography for residual oxide layer on GaAs(100) was carried out by UHV-STM. For comparison, we also performed STM lithography on samples without pre-thermal treatment. Aiming at achievement of small size pattern, lithography were performed by various bias voltages from 5 to 20V and tunnel currents from 2.5 to 10 nA for 10-30 sec. It was found that threshold is present in electric power [bias voltage \times tunnel current] to remove surface oxide by lithography. Control of the size of lithography area was improved by lowering bias voltage. Compared with lithography for samples with pre-thermal treatment, precise control of lithography area was difficult on samples without pre-thermal treatment, though lithography pattern on them could be fabricated by lower bias voltage. This means pre-thermal treatment induces hardening of oxide layer. By using optimized conditions, very fine patterning, square areas less than 25 \times 25 nm², was successively achieved. Simulations of field emission from STM tips based on the Fowler-Nordheim equation were also performed and comparison with the size of experimental lithography results will be discussed.

SESSION C6: Nanoimprint and Templated Lithography

Chairs: Rod Kunz and Eric Lin

Wednesday Morning, December 1, 2004

Republic A (Sheraton)

8:30 AM *C6.1

3-Dimensional Nanoimprinting. Stella W. Pang, Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, Michigan.

Unique capabilities of nanoimprinting have been demonstrated for 3-dimensional patterning. These include generating multiple layer polymer stacks, 3-dimensional structures, channels, cavities, conformal coating, as well as patterning inside trenches. For successful nanoimprinting of these micro- and nano-structures, proper surface treatments, imprint temperature and pressure, polymer materials, and addition of plasticizers are important. A new imprinting technique called reversal imprinting was developed. In reversal imprinting, a polymer film is spin-coated onto a mold and then transferred to a substrate. Depending on the applications, the mold can have patterns or it can be flat, and either hard or soft molds can be used. Three distinctive patterning modes are obtained, including 'continuous film transfer over microstructures', 'film transfer to both trenches and protrusions', and 'film transfer to protrusions only'. With 'continuous film transfer over microstructures', nanochannels, nanocavities, and 3-dimensional nanostructures can be produced. For 'film transfer to both trenches and protrusions', forming conformal coatings and patterning along the sidewalls, tops, and bottoms of the trenches are possible. Using 'film transfer to protrusions only', inking occurs and polymer stacks with various polymer layers and no intermixing can be achieved. Reversal imprinting provides the advantages of simplicity, versatility, and high resolution. Addition of plasticizer in polymer lowers temperature and pressure needed for imprinting. Besides generating 3-dimensional structures, reversal imprinting also allows flexible or curved substrates to be patterned. These unique patterning capabilities are difficult to accomplished using conventional patterning techniques.

9:00 AM C6.2

Fabrication of Complex Three Dimensional Nanostructures with High Resolution Conformable Phase Masks and Its Applications. Seokwoo Jeon^{1,2}, Jangung Park^{1,2} and John A. Rogers^{1,3,2}; ¹Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Beckman Institute and Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois; ³Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

High resolution, conformable phase masks provide a means to fabricate, in an experimentally simple manner, classes of three

dimensional (3D) nanostructures that are technologically important but difficult to generate in other ways. In this approach, light passing through a phase mask that has features of relief comparable in dimension to the wavelength generates a 3D distribution of intensity that exposes a photopolymer film throughout its thickness. Developing away the unexposed regions yields a complex 3D polymer nanostructure defined by the distribution of intensity. We briefly describe the technique, outline a full rigorous coupled wave analysis of the optics, and illustrate its use in building a broad range of nanostructures. Nanoporous 3D filters, chaotic mixers and chromatographic materials integrated into microfluidic channels illustrate an application of this technique that might be useful for micro total analysis system or lab on a chip devices. Chemical vapor deposition of SiO₂ using the 3D polymer structures as templates yields silica structures that are useful in photonics and micro electromechanical systems.

9:15 AM C6.3

NIL Techniques Applied to Transfer Printing onto Flexible Substrates.*, Daniel R. Hines¹, V. Ballarotto³, S. Mezheny¹, M. Breban¹ and E. D. Williams²; ¹Laboratory for Physical Sciences, University of Maryland, College Park, Maryland; ²Physics Department, University of Maryland, College Park, Maryland; ³Laboratory for Physical Sciences, College Park, Maryland.

We have developed transfer printing (TP) techniques based on nano-imprint lithography (NIL) processes to print metal electrodes and organic films onto flexible substrates. We have defined conditions for transfer printing of an organic electronic material (pentacene) from an SiO₂ substrate onto a number of flexible substrates including PET, PVC-vinyl and PMMA, as well as documenting a number of materials onto which transfer (without chemical preparation) does not occur. We have also transferred Au patterns successfully to flexible substrates without any pre-treatment of the gold film. In addition, we have found that in cases where specific transfer steps are unfavorable (e.g. pentacene does not fully transfer to a Au surface), we can successfully accomplish a transfer of a pre-assembled multilayer. This has been demonstrated using concurrent transfer of both the pentacene and gold films of a top-electrode organic thin film transistor. Transfer of pre-patterned 200 nm lines is readily achieved, with embedding of metals into the plastic substrate possible under controlled imprint conditions. We will compare the use of traditional TP from patterns on flat surfaces with the use of NIL masks covered with the transfer material. In addition we will report on transistor characteristics of devices fabricated using transfer printing sequences. *Supported by the Laboratory for Physical Sciences.

9:30 AM C6.4

Antireflective Transparent Polymers by One Step Nanostructuring. Alfons Fischer¹ and Norbert Beyer²; ¹Mater. Sci. Eng. II, University of Duisburg-Essen, Duisburg, Germany; ²AlCove Surfaces GmbH, Gladbeck, Germany.

The concepts of enhancing desired surface properties by nanostructured imprinting methods will be described as a perfect example of an interdisciplinary approach in physics, engineering and chemistry. This methods will serve the steadily increasing demands of antireflective displays e.g. for mobile communication devices, automotive interior, lenses for various applications. If one thinks about improved light transmission through transparent medias together with a suppressed reflection the method of roughening the surface cannot be applied since scattering not only reduces light reflection but also drastically reduce directed light transmission accompanied with randomly propagating light causing disturbing fogging. Nevertheless surface topographies being smaller than the wavelength of visible light reveal a solution. Air is the predominant outer environment to all these applications. Thus, above the surface the refractive index of air is valid and below the surface that of the substrate material. Now the nanotopography brings about a gradual change (compared to a flat surface) in refractive index and causes light to penetrate into the substrate almost without being scattered or reflected. The challenge is simply to structure a surface on the nanometer scale, similar to the prominent Moth-Eye-structure. Different approaches have been tested so far and only few are suitable for serial production. The most intriguing feature of nanoporous alumina is the adjustable pore geometry. The benefits of these alumina templates are: Pore formation by a self-assembling electrochemical process, adjustable diameter of the surface structure from 50 nm to 500 nm, adjustable height of the surface structures from a few up nm to μm , chemically inert and wear resistant ceramic surface, complex, three dimensional geometries can easily be structured. A blank sample of PMMA does show a light transmission of approx. 91 % over the complete spectral range. With a 120 nm surface structure this light transmission can be enhanced by 4% over the complete spectral range for each structured side, 99% transmission for a double side structured sample can be achieved. The same observation holds for other transparent polymers like PC, PS, or different copolymers. Besides using tools of this type in injection

moulding it is possible as well to cast or to imprint the surface structure into a desired material on a larger scale. Casting can be applied to any kind of curable system. For example UV-Lacquer, epoxy resins or polydimethylsiloxane. Direct structuring of glass is not possible, but by coating the surfaces with a sol-gel, transferring the structure of the nanoporous alumina and curing the sol-gel afterwards leads to the desired surface structure.

10:15 AM *C6.5

Nanoimprint Lithography: Basic Materials Science for High Fidelity Patterning. Christopher L. Soles¹, Ronald L. Jones¹, Ronald M. Reano² and Stella W. Pang²; ¹Polymers Division, NIST, Gaithersburg, Maryland; ²Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

Nanoimprint lithography (NIL) has emerged a high-resolution tool for printing physical patterns into polymeric film or resist in a rapid and cost-effective manner. State of the art imprints demonstrate that line widths as small as 5 nm are feasible. This is a significant advance in terms of rapid patterning technology given that optical lithography struggles to produce patterns smaller than 90 nm in a reliable manner. However, there are several problems introduced, or at least magnified, by the increased resolutions now feasible with NIL. First, simple pattern shape metrology becomes non-trivial when the minimum dimensions fall below 90 nm. In other words, it becomes increasingly difficult to quantitatively assess the fidelity with which the pattern in the mold is transferred to the polymeric resist. Second, the minimum feature size is quickly becoming commensurate with the size of a single polymer molecule (assuming a Gaussian-like random coil). This implies that the molecular conformations, and presumably the resulting physical properties, in the imprinted structures will be distorted as compared to the bulk material. It remains to be seen how these conformational distortion affect the fidelity of the pattern transfer process and the resulting stability of the final resist structures. To address these questions, Critical Dimension Small Angle X-ray Scattering (CD-SAXS) is introduced as a metrology to characterize the line shape profiles in nanoimprinted structures. CD-SAXS is a transmission scattering technique, meaning that pattern shapes in the mold can be directly compared to the resulting pattern shapes in the final imprinted structure to quantitatively assess the fidelity of pattern transfer. This fidelity will be mapped out as a function of basic materials science and processing parameters such as polymer architecture, molecular mass, and imprinting temperatures. Next, we will explore the use of CD-SAXS to track the long term and environmental stability of nanoimprinted structures. It is anticipated that the molecular distortions induced during the imprint process will have a propensity to relax over time and with temperature. The impact of this relaxation on pattern quality will be explored.

10:45 AM C6.6

Nanocontact Molding: Polymeric Materials Issues for Imprint Lithography for High Resolution Pattern Transfer.

Kenneth R. Carter, IBM Almaden Research Center, San Jose, California.

Imprint Lithography (IL) is being examined as an alternative to photolithography for the manufacture of nanostructured materials for use in electronics, photonics and proteomics. Imprint lithography can be roughly broken into two areas: (1) so-called soft lithographic techniques such as solvent assisted micro-molding (SAMIM), micro-molding in capillaries (MIMIC) and microcontact printing (MCP), and (2) rigid imprint techniques such as nano-contact molding (NCM), 'step and flash' imprint lithography (S-FIL), and nanoimprint lithography (NIL). The ability to fabricate sub-100 nm features using relatively simple and potentially inexpensive contact image transfer processes makes IL an extremely attractive technology. While great advances have been made in the availability of commercial imprint lithographic tools, materials development is still in its infancy. It is becoming increasingly clear that new materials are needed to advance IL methodologies to their ultimate performance limits. It is clear that structure property relationships, chemical functionality, adhesion and release are issues that will dictate the usefulness of any material and hence process. Polymeric materials play a key role in NCM techniques, both as mold materials as well as patternable layers (imaging resists or functional active structures). The use of photopolymerizable materials allows for a great diversity of materials used in IL. Herein, we report our latest results in the development of mold-making materials, imaging resists and molded functional nanostructures.

11:00 AM C6.7

Determination of Modeling Parameters for Nano-Imprint Lithography Process Control. David A. Mendels, Alexandre Cuenat and Nicolas M. P. Evanno; Applied Nanotechnologies, National Physical Laboratory, Teddington, Surrey, United Kingdom.

Suitable modeling tools for the nano-imprint lithography (NIL) process are needed to achieve control of the embossed shape and

residual layer thickness. The determination and optimization of process windows, a robust process and most importantly low cycle times are key requirements for industrial applications. Due to the relative dimensions of the stamp and the embossed shapes, a sub-modeling approach based on finite elements (FE) is used to transfer accurately boundary conditions on the stamp (e.g. clamps, pressure distribution, wafer waviness), the repeating units, and details within the units. Integration of the millimeter (stamp wafer) and tens of micrometers (repeating unit) scales is derived from MEMS modeling. By opposition, nano-scale modeling of the embossing process remains a challenge, due its many unknowns, such as the boundary conditions and the materials behavior at these scales. The processing and post-processing of thin polymer films by NIL presents subtle differences with macroscopic hot embossing. The polymer is spin-coated on a silicon wafer, its solvent is evaporated, and the resulting thin layer is heated to above its glass transition temperature, or its melting temperature, before being embossed. The thickness of the polymer layer typically ranges between a few nanometers and tens of micrometers. Main differences with macro-scale behavior are associated with the very low thickness of the polymer and the small lateral dimensions of the stamp. The unknown inputs for NIL modeling are the constitutive behavior of the polymer layer and its interactions with the tool. Starting with the interactions, the adhesion and friction mechanisms between the flat indenter walls and the polymer are resolved by AFM and FFM measurements. At the nano-scale, it is not necessary to deal with the sharp edges of the stamp as Cauchy singularities, as the curvature of the edge is within the same order of magnitude as the stamp. As viscoelastic properties are strongly coupled with the stress state, the constitutive behavior of the polymer is ideally determined independently of any tool interaction. Consequently, a modified quartz crystal microbalance (QCM) apparatus is used to determine the storage and loss moduli over a wide range of temperatures. Both contact and materials properties are further used in a FE model, which renders most of the features of the process. Finally, post-processing also needs resolving: because the stamp only remains a short time in the polymer layer, both elastic and viscoelastic recovery are bound to happen when it is removed. One additional source of loss of dimensional stability is cross-linking, where the polymer is thought to experience considerable shrinkage that may be anisotropic due to the residual stress state of the embossed layer. This issue, together with the advances in process modeling described above, will be introduced and compared to state of the art experimental processes.

11:15 AM C6.8

Novel Chemical Approach for Achieving High Fidelity, Nano-Scale Soft Lithography by Developing a New Class of PDMS Stamp Materials. Kyung M. Choi¹ and John A. Rogers^{1,2};

¹Bell Labs, Lucent Technologies, Murray Hill, New Jersey; ²Materials Science and Engineering, University of Illinois at UC, Urbana, Illinois.

Since industry has been seeking precision nano-devices with enhanced performance at low cost, developments of new materials and advanced fabrication techniques are desperately required. Soft lithography has been widely used in the replication and fabrication of small features as a low cost alternative to conventional photolithography. However, commercial stamp materials used in current soft lithography are limited in their applications to nano-resolution lithography due to their low moduli since conventional PDMS materials are initially produced for other purposes. Here we developed a new class of PDMS stamp materials, to overcome the limitations and thus to extend this technology to the high fidelity nano-scale regime. For the molecular modification, we inserted into stamp materials with diverse organic functionalities such as photocurable, rigid, and fluoroalkyl-groups to create desired properties, which are enhanced mechanical stiffness, good physical toughness, photocurability, stress-free systems, high hydrophobicity, and low polymerization shrinkages. Since the resolution of soft lithography significantly relies on the performance of stamp materials, we demonstrated its unique capabilities for the case of nano-striated features of 300 nm width and 600 nm height in photoresist, which is one of the most challenging 'nano-patterning tasks' in advanced soft lithography. We also demonstrated here 'elastomeric photopatterns' in the 5 nm resolution range using the new photocurable, stiff PDMS prepolymer. Since microfluidic channel materials based on those conventional PDMS materials swell in most organic solvents, here we synthesized a new version of highly fluorinated, photocurable PDMS prepolymers to bring high hydrophobicity for our microfluidic applications.

11:30 AM C6.9

Rapid Flash Patterning for Sub-100 nm Structures.

Hong H. Lee, Hyunsik Yoon, Jun-ho Choi, Se-young Park, Soonmin Seo and Joonhyung Park; Chemical Engineering, Seoul National University, Seoul, South Korea.

Sub-100 nm structures can be fabricated in tens of seconds with an aspect ratio much larger than unity by rapid flash patterning (RFP)

presented here. A thin film mold (0.1–0.2 mm thick) of a photocurable polyurethane acrylate liquid (PUA) is placed on the polymer layer that has been spin-coated onto a substrate and dried. The film molds were replicated from the patterns made by photolithography or electron-beam lithography with a poly(ethylene terephthalate) (PET) as the backplane support. To assure a uniform pressure distribution when pressed, a poly(dimethylsiloxane) (PDMS) block is placed on the film mold followed by a glass plate, onto which pressure is applied. While this arrangement yielded uniform patterning results over an area of 1 cm² at the typical applied pressure of 3 to 4 bars, similar arrangement with a larger mold should give pattern uniformity over a larger area. In the pressed state, a halogen lamp in infra-red (IR) range is flashed for a short period of time, typically tens of seconds. The temperature reached is typically around 260 °C. During the heating, the polymer is primarily heated because the film mold and PDMS block are semi-transparent. After a few minutes of cooling, the pressure is relieved, followed by removal of the glass, the PDMS block and the film mold, leaving behind a patterned polymer layer on the substrate. With this technique, 80 nm wide lines of poly(vinylalcohol) (PVA) with an aspect ratio in excess of 5 were successfully patterned on the silicon substrate. One-step reactive-ion etching (RIE) was carried out with the patterned polymer resist to etch into the underlying silicon wafer. Unlike other unconventional methods, the substrate surface can be made exposed and the resulting pattern height is sufficiently high for subsequent etching of the substrate. The essence of RFP lies in the use of a flexible, rubbery mold. When a hard mold is used, the substrate surface does not get exposed because dewetting cannot take place due to the rigidity of the hard mold. The PUA mold has a Young modulus of 0.3 GPa that is high enough for fine patterning and yet low enough for flexibility. The RFP is perhaps the first unconventional general purpose patterning method that can make the substrate surface exposed and yet the resulting film is sufficiently thick enough for subsequent etching.

SESSION C7: Scanning Probe and Direct Write
Lithography
Chairs: Marie Angelopoulos and Eric Lin
Wednesday Afternoon, December 1, 2004
Republic A (Sheraton)

1:30 PM C7.1

Dip-pen Nanolithography Stamp Tips. Hua Zhang, Robert Elghanian, Linette Demers, Nabil Amro, Sandeep Disawal and Ray Eby; NanoInk, Chicago, Illinois.

A simple and novel method for fabricating polydimethylsiloxane (PDMS)-coated dip-pen nanolithography (DPN) stamp tips was developed. These kinds of probe tips adsorb chemicals ("inks") easily and allow one to generate molecule-based patterns in a conventional DPN experiment. The generated patterns also can be imaged with the same DPN stamp tips. This DPN method is a type of scanning probe contact printing but provides the ability to generate higher resolution structures than one can obtain with a more conventional contact printing techniques, which thus far have only enabled micron scale patterning. Sub-100 nm resolution patterning with 16-mercaptohexadecanoic acid as an ink is demonstrated with these novel tips and is comparable to what one can obtain with a conventional ink-coated Si₃N₄ probe tip. Proof-of-concept is also demonstrated with 1-octadecanethiol (ODT), dendrimers, cystamine and inorganic salts as inks.

1:45 PM C7.2

Thermal Control in Dip Pen Nanolithography.

Paul E. Sheehan¹, William P. King² and Lloyd J. Whitman¹; ¹Naval Research Laboratory, Washington, District of Columbia; ²Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Although it has been widely assumed that Dip Pen Nanolithography (DPN) requires a water meniscus to transfer ink from an AFM tip to a surface, we have shown that transfer can occur under xeric conditions, a method we call "dry deposition." Our recent studies of dry deposition have led to a number of insights into how DPN can be extended beyond "wet" inks. For example, deposition should be possible at high temperatures (i.e., above the boiling point of water) and, thus, temperature could be used to control deposition. We have utilized a heated atomic force microscope (AFM) cantilever tip to control the deposition of a solid organic "ink". The ink, octadecylphosphonic acid (OPA), melts at 98 °C and self-assembles on mica, the substrate. Evaporation was used to coat OPA onto a cantilever with integrated microheaters. When the cantilever temperature was below 98 °C, no deposition was detected. At 98 °C slow deposition was seen, but only after raising the temperature to 122 °C was deposition robust. Thermal DPN (tDN) enhances traditional DPN in many ways. First, it allows exquisite control over

writing-deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. Secondly, the inks used have lower surface mobilities once cooled and so are able to achieve higher spatial resolution. Thirdly, imaging with a cool tip does not appear to contaminate the surface. This allows in situ confirmation of the deposited pattern without fear of contamination. Finally, tDPN expands the range of useable inks—current work with electronically active molecules that have high melting temperatures will be presented.

2:00 PM C7.3

Comparison between Contact and Non Contact Mode in AFM Local Anodisation for InP Patterning. Bremont E. Georges and Tranvouez Edern; LPM, INSA Lyon, Villeurbanne, France.

The miniaturization of electronic or optoelectronic components induce a perpetual increasing of lithography cost. In the future, this increasing will be accelerating by the emergency of the deep-uv or the x-ray lithography technique. In this context, alternatives techniques, like lithography based on Atomic Force Microscopy (AFM) or electronic microscopy (e-beam) could be a good solution to develop demonstrated devices in advance on heavier technologies. These techniques come to be mature and "easily" allow to obtain nanoscale writing. The weakness of writing velocity could be compensated by a complementary use of traditional lithography techniques which allows nanocomponents integrating. Although the importance of InP in telecommunication technology, the AFM nanolithography has been rarely investigate in order to fabricate nanophotonic devices. We report, here, the InP local oxidation using AFM. The main purpose is to control in nanoscale writing process which allows to either isolate or/and organize nanostructures. Two approaches are explored. The first method consists to apply a constant potential between the probe and the substrate in contact mode. The second method proposes an original technique combining an AFM intermittent contact mode with an alternating voltage. These two methods are implemented on an AFM DI3100 working under controlled atmosphere in term of gas composition and hygrometry. The first realized patterns are solid lines (figure 1a) ranging from 60 nm to 300 nm in width and from 4 to 30 nm in high. These lines enabled us to analyze the growth of oxide formed according to the applied voltage as well as the lithography velocity. The second used patterns are dots (figure 1b) for which the diameter and the height are ranged respectively from 15 to 250 nm and from 1 to 15 nm. Therefore, it is possible to characterize the influence of applied voltage and time exposition onto oxidation process. The homogeneity of these two oxidation techniques could further be analyzed. The results performed in contact mode exhibits an oxide growth linear law as function of applied voltage (figure 2a) but also a logarithmic evolution with velocity and oxidation time (figure 2b) in agreement with predicted nanoanodisation mechanisms [3]. This mode is also characterizing by a poor homogeneity with 50nm maximum lateral resolution. In intermittent contact mode, these results are more contrasted and highlight saturation for low velocity (below 0.1 $\mu\text{m.s}^{-1}$) and a good resolution (15nm). Finally to characterize volume aspect of these oxides, the samples were selectively etching with hydrofluoric acid. The growth is symmetric from the surface ("surface" oxide accounts for 40 to 52 % of total volume). We will discuss and explain all our results in terms of space charge behavior during lithography and present possibilities for InAs Quantum Dots controlled growth on InP.

2:15 PM C7.4

Electrochemical Nanolithography on PVK Films Using AFM. Suresh Valiyaveetil^{1,2}, Jagadesan Subbiah^{1,2} and Rigoberto Advincula³; ¹Chemistry, National University of Singapore, Singapore, Singapore; ²NUS Nanoscience and Nanotechnology Initiative, National University of Singapore, Singapore, Singapore; ³Chemistry, University of Houston, Houston, Texas.

The ability of patterning polymeric films with interesting electronic properties at nanoscale has attracted great attention owing to the potential of opening up a new platform of technologies towards developing nanodevices in areas such as data storage, optoelectronics, displays, and nanosensors. Poly(vinylcarbazole) (PVK) has interesting properties and it can be polymerized by both radical and electrochemical (cationic) methods. The polymer obtained via electrochemical oxidation is charged and show conducting properties. In this presentation, we describe the electrochemical nanolithographic method to fabricate nanostructures on a substrate.

2:30 PM C7.5

Enhanced Etching Resistance of Nanocomposite Resist for Scanning Probe Lithography. Daniel (Ching-Shih) Chiang, Philip (Zifeng) Lei and Rudy (See-Ru) Hsia; Materials and Mechanical Engineering, Washington State University, Vancouver, Washington.

We have developed nanocomposite resists by incorporating C60 or carbon nanotubes (CNT) into conventional electron resist in order to

realize an ultra-thin resist process for practical nanometer scanning probe lithography. Enhanced etching resistance and sub-100nm line width of the new resists is shown from the preliminary studies. We will discuss the difference of the etching resistance, the pattern contrast and the sensitivity between the resists incorporating C60 and the resists incorporating CNTs.

3:15 PM C7.6

Formation of Conducting Polymer Nanostructures from Aniline, Pyrrole and 3,4-Ethylenedioxythiophene using Electrochemical Dip-Pen Nanolithography. Shaun Filocamo¹, Benjamin Maynor², Chad Immoos², Jie Liu² and Mark Grinstaff¹; ¹Department of Chemistry, Boston University, Boston, Massachusetts; ²Chemistry, Duke University, Durham, North Carolina.

The development of new patterning techniques in the sub-100 nm range has become increasingly important as the feature size for devices surpasses the 100 nm barrier. Of the patterning materials available, conducting polymers are one class of organic materials that are of interest since these polymers exhibit thermal and environmental stability, and ease of processing, properties that have been utilized for device applications at the micron scale in tandem with or as an alternative to inorganic materials. Traditional lithography processes require robust materials that can withstand high energy particles, all but excluding the patterning of organic materials using these techniques. We have developed an electrochemical dip-pen nanolithography (E-DPN) technique to draw nanolines from conducting polymer precursors, such as aniline, pyrrole and ethylenedioxythiophene (EDOT). We are able to draw polymer lines and interconnects and show the lines are chemically different from SiO₂, despite using voltages at which surface oxidation would be a competing reaction. To illustrate the structural integrity of the monomer unit is maintained, we immersed a poly(EDOT) line in a HAuCl₄ solution and added a mild reducing agent. Upon reimaging, the Au nanoparticles formed congregated preferentially on the polymer line, consistent with previously reported observations that Au nanoparticles can nucleate on polythiophene. We will present those findings as well as the mechanical and electrochemical properties of these nanowires.

3:30 PM C7.7

High-Throughput Methods for the Optimization of Z-lift Electrostatic Lithography. Shane Juhl¹, Pavel Paramonov², Dave Phillips¹, Sergei Lyuksyutov² and Richard Vaia¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio; ²Departments of Physics and Polymer Engineering, The University of Akron, Akron, Ohio.

Scanning probe microscope based lithographic techniques hold promise for a wide range of applications including semiconductors, MEMS, and data storage. Z-lift electrostatic lithography creates variable height structures on a wide range of thin polymer and other organic surfaces through local heating by current flow and subsequent attraction of the softened polymer to the biased AFM tip similar to the atomic force microscope electrostatic nanolithography (AFMEN) process. Mechanically drawing or depressing the softened polymer controls structure aspect ratio and heights through changing the cantilever height (z-lift) during application of voltage. The plethora of processing parameters makes optimization of feature formation difficult. Various aspects such as current and voltage doses, film thickness, cantilever stiffness, and z-lift height, rate, and step are explored using high-throughput methodology. Structure height formation relies mainly on and is proportional to the z-lift value, however, only a narrow range of voltages produces reproducible structures for any given film thickness. Structure densities of a terabyte/cm² made with controllable heights ranging from 0 to over 10 nm are produced on a 40 nm thick polystyrene film using negative 36 V by varying the z-lift on a 0.35 N/m cantilever from negative 20 nm to positive 400 nm.

3:45 PM C7.8

Beam Lithography of Ordered Quantum Dot Arrays by Focused Ion Beam Lithography. Yingge Du¹, James F. Groves¹, Igor Lyubinetsky² and Suntharampillai Thevuthasan²; ¹University of Virginia, Charlottesville, Virginia; ²Pacific Northwest National Laboratory, Richland, Washington.

As the dimensions of electronic devices continue to scale down, traditional lithography is challenged to enable ever higher levels of nanoscale feature integration. In recent years focused ion beams have begun to be used as versatile maskless lithography tools that enable nano-scale feature definition. In this work, an FEI series 200 focused ion beam was used to implant localized dosages of Ga⁺ into a SrTiO₃ (100) substrate at a beam energy of 30 keV. The FIB implants generated surface topography with lateral dimensions of 30-70 nm and implant spacings of 83 nm to 170 nm. Carefully controlled ion dosages were implanted into different regions of the substrate, and the

morphology changes were characterized by atomic force microscopy. During subsequent substrate annealing, the implanted spots evolved to well-defined, square-based holes because of recrystallization. Following substrate patterning, annealing, and cleaning, the FIB template served as the guide for fabrication of ordered quantum dot arrays. Oxygen plasma assisted molecular beam epitaxy was used to grow Cu_2O quantum dots on the FIB patterned SrTiO_3 substrates. In-situ X-ray photoelectron spectroscopy and Auger electron spectroscopy analysis demonstrated that the final phase of the nanodots was Cu_2O . Under selected conditions, the nanodots preferentially nucleate inside the holes and then grow in size on top of the FIB induced topography. Observation reveals that one quantum dot grows on each FIB nanoscale topographic feature. Initial analysis has been performed on the fabricated samples to quantify quantum dot size, size distribution and inter-dot spacing, important characteristics for next generation nanoelectronic applications.