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13. ABSTRACT *(Maximum 200 words)*

Among the more notable accomplishments during the course of this contract we identil$ the following results: o We have used diblock copolymers to transfer nanoscale periodic patterns to substrates. The nanopatterns have been transferred both in the form of etched holes and in arrays of metal dots. This has been performed without the need for silicon nitride layers or multi-layered resists. o We have conducted experiments using a closed-loop MM to measure the coefficient of thermal expansion (CTE) of a reference material. We have found that the piezo scanner non-linearity (0.2 %) is unacceptably large for metrologic MM Moire intertbrometry. We have ordered a new closed-loop MM that incorporates a flexure-based scanner with a nonlinearity of 0,05 %. The new instrumentation will allow us to overcome the piezo non-linearity difficulties, d We have demonstrated a method for utilizing nanomasks for pattern transfer to an arbitrary substrate via an intermediate transfer layer (ITL). This approach is distinct from the technique of applying the nanonasks directly to the sur&ce to be patterned. The ITL is a layer of a resist-like material into which the bionanornask pattern is transferred before it is then transferred to the substrate.

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Parallel Fabrication and Optoelectronic Characterization of Nanostructured Surfaces

AFOSR Grant No. F49620-99-1-0105

Final Report

June, 30, 2002

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Original Objectives

- Monte Carlo simulation of nanocluster array formation in confined geometries
- nanocluster array formation and characterization using III-V materials
- tunable nanomask development

Status of Effort

Among the more notable accomplishments during the course of this contract we identify the following results:

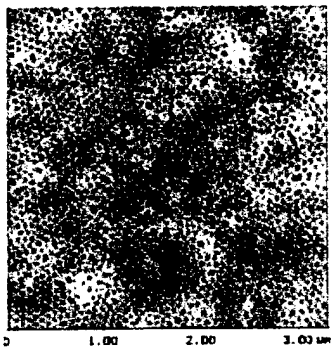
• Nanopattern Transfer from Solvent-Annealed Diblock Copolymers

We have used the techniques we've developed for self-assembled biological templates and applied them to diblock copolymers to transfer nanoscale periodic patterns to substrates. The nanopatterns have been transferred, using inductively coupled plasma (ICP) etching, both in the form of etched holes and in arrays of metal dots (using electron beam evaporation). As distinct from other published work, this has been performed without the need for silicon nitride layers or multi-layered resists.

Block copolymers consist of two chemically distinct polymer chains that are covalently linked. When dissolved in a solvent and spun onto a substrate, the polymer chains phase separate to form chemically distinct nanometer-scale domains. The size and morphology of these domains is determined by the size and composition of the polymer chains. Upon annealing above the glass transition temperature of the polymers, the nanometer-scale domains spontaneously rearrange to form micron-scale grains with local nanoscale periodicity. These micrograins can have a variety of symmetries (i.e., lamellae, cylinder, or spheres) depending upon the copolymer system used and the thickness of the thin film.

However, once a polymer system and a film thickness are chosen. *thermal* annealing always produces the same morphology. In contrast, by *annealing in solvent vapors*, we've demonstrated a method of annealing that allows us to create *different* morphologies from the same choice of polymer and film characteristics. The morphology of the resulting film depends only upon the solvent used for annealing. For the work shown here, we used a polystyrene-b-polyisoprene (PS-b-PI) diblock copolymer.

The figure shows a 35 nm thick film of polyisoprene-b-polystyrene (PI-b-PS) which phase separates into an hexagonal array of polyisoprene cylinders in a polystyrene matrix after annealing in MEK vapors.



We've transferred this pattern into a Si substrate by ICP etching until the film is completely removed. Because the etch rates of the two polymers are similar, the surface relief of the etched substrate is only a few nanometers. To improve on this, we have selectively removed one of the polymers before etching by exposing the copolymer film to ozone in an aqueous environment. The ozone treatment makes the polyisoprene water-soluble and cross-links the polystyrene, leaving an array of cylindrical holes in the polystyrene film. Etching of this film, produces a nanoscale array of holes in the substrate with improved aspect ratio.

At present, two issues limit the depth of etched holes created with diblock copolymer masks. The first is the etch rate of the copolymer. As one etches the substrate through the holes in the copolymer mask, the copolymer is also being etched. When the copolymer is completely etched away, the depth of the holes stops increasing. The second limitation arises from lateral etching. Once the lateral etching widens the holes and they bridge together, the depth of the etched holes cannot be increased.

In our continuing work, we plan to eliminate the first limitation by coating the copolymer with a thin layer of Cr as we do with our biological/protein crystal masks. Initial experiments have shown that a 2 nm thick layer of Cr deposited on a copolymer film will allow us to etch 500 nm or more into a Si substrate with no visible signs of mask degradation. We plan to address the issue of lateral undercutting using sidewall passivation. We will etch the substrate with a fluroine-based chemistry and will protect the sidewalls with a thin layer of a fluorocarbon polymer and block the thermal etching of the fluorine. On the horizontal surfaces, energetic ions will remove the fluorocarbon

polymer and allow the surface to be etched. We will cycle back and forth between etching and passivation, etching deeper during each cycle. This technique is used very successfully for micron-scale MEMs work, however, this has not been accomplished at the 10-nm length scale. The difficulty will lie in depositing the correct amount of passivation to protect the sidewalls without filling up the holes and with etching for the correct amount of time to preserve anisotropic etching.

• Ultrahigh Resolution Scanning Probe Microscope Gratings for Moiré Interferometry

As previously discussed in a progress report, the goal of this effort is to use coated protein crystals as ultrahigh resolution gratings in conjunction with a scanning probe microscope (SPM) to generate Moiré interferometry patterns for ultrahigh resolution measurement of parameters such as thermal coefficients of expansion. This technique could be used to examine interconnects, vias, and other features which can become vulnerable to fatigue failures due to materials' properties and compatibility. The microelectronics industry requires techniques that can measure displacements, identify failure locations and mechanisms, and provide thermomechanical data to models at submicron size scales to optimize design. The techniques that have been developed include electron-beam moiré, moiré interferometry, digital image correlation, and speckle interferometry. However, none of these techniques is presently able to measure displacements as small as 5 to 10 nm, as is required to calculate strains in on-chip vias and interconnects, or in chip-on-glass packages.

Since our last report, we have conducted extensive experiments using a closed-loop Thermomicroscope AFM at NIST to measure the coefficient of thermal expansion (CTE) of a reference material (typically either gold or silicon). These experiments are necessary to evaluate the piezo non-linearity, drift, creep, and hysteresis of the instrument.

Our results clearly indicate that we have a systematic error that is over-shadowing any real expansion data from the samples. The problem lies in the specifications for the Thermomicroscope AFM, specifically, the scanner non-linearity which is 0.2 %. When scanning a 100 nm pitch grating at 256 lines/scan, one must scan a 25.6 μm x 25.6 μm area to generate the proper moiré fringes. A non-linearity of 0.2 % over a 25.6 μm distance yields an error of ~ 50 nm or a half of a fringe. Assuming that the sample is cycled over a 75 C range, this half of a fringe error gives a CTE error of ~ 30 ppm which is unacceptably large for metrologic work.

We have now placed a purchase order for a new closed-loop AFM that incorporates a flexure-based scanner which is quoted to have a nonlinearity of 0.05 %. We have also placed a purchase order for an optical interferometer with a resolution of 0.3 nm to maintain the calibration of the closed-loop flexure stage scanner. We expect that the new instrumentation will allow us to overcome the piezo non-linearity difficulties and this will be determined by an acceptable measurement of the CTE of a reference material. Once this is accomplished, we will return to the focus of this work, which is to use coated

Personnel Supported During this Contract:

Faculty:	Dr. Kenneth Douglas
Post-Docs:	Dr. Thomas A. Winningham
Graduate Students:	Steven Whipple
Other:	None

Publications

"Pattern Transfer from Solvent-Annealed Diblock Copolymers," Thomas A. Winningham, Adam Harant, Steven G. Whipple, C. Bowman, Noel A. Clark, and K. Douglas (to be submitted to Applied Physics Letters, 2002).

"A Simple Preparation of Self-Assembled Monolayers on Float Glass Using Alkyltrialkoxysilanes," D.M. Walba, C.A. Liberko, E. Körblova, M. Farrow, T. Furtak, K. Douglas, S.D. Williams, A.F. Klittnick, and N.A. Clark, (submitted to Langmuir, 2002).

"Pattern Transfer from a Biomolecular Nanomask to a Substrate via an Intermediate Transfer Layer," Thomas A. Winningham, Steven Whipple, and Kenneth Douglas, J. Vac. Sci. Technol. **B 19**, 1796 (2001)

"Validation of Scanning Probe Moiré Technique Using the CTE of Gold", Drexler, E.S., and Winningham, T.A., Proceedings of the Society for Experimental Mechanics, Bethel, CT, pp. 387 - 390 (2001).

Interactions/Transitions

participation/presentations at meetings, conferences, seminars, etc.

"Massively Parallel Nanofabrication Using Biological Masks," Physics Departmental Colloquium, University of Central Florida, Orlando, Florida (April, 2002).

"Massively Parallel Nanofabrication Using Biological Masks," Physics Departmental Colloquium, University of Louisville, Lousiville, Kentucky (April, 2002).

"Pattern Transfer and Amplification Using Diblock Copolymers," Ferroelectric Liquid Crystal Materials Research Center Research Review, Department of Physics, University of Colorado, Boulder, Colorado (November, 2001).

"Validation of Scanning Probe Moire Technique Using the CTE of Gold", Drexler, E.S., and Winningham, T.A., Society for Experimental Mechanics Annual Conference on Experimental and Applied Mechanics, Portland, Oregon (June, 2001).

"Formation of hybrid SiC/Si and SiC/SiO2/Si wafers by oxygen implantation, wafer bonding, and etching," J.T. Torvik , R. Krutsinger, B.J. Van Zeghbroeck, T.A. Winningham, K. Douglas, and W. Wesch., 43rd Electronic Materials Conference (TMS, The Minerals, Metals, and Material Society), Notre Dame, Indiana (June, 2001)

Invited: "Quantum Dot Arrays from Biological Etch Masks," First International Conference on Molecular Electronics and Bioelectronics, Japanese Society of Applied Physics, Hyogo, Japan (March, 2001).

Invited: "Biomolecular-Derived Quantum Dot Arrays," Physics and Electrical Engineering Departmental Colloquium, University of Colorado, Colorado Springs (March, 2001).

Invited:"Quantum Dot Arrays from Biological Etch Masks," National Institute for Standards and Technology (NIST) Materials Reliability Division Seminar, Boulder, Colorado, (August, 2000).

Invited: "Quantum Dot Arrays from Biological Etch Masks," Oak Ridge National Laboratory (ORNL) Advanced Microsystems Group Seminar, Oak Ridge, Tennessee (September, 2000).

consultative and advisory functions to other laboratoraties and agencies
None

transitions
None

New Discoveries, Inventions, or Patent Disclosures

"Ultrahigh Resolution Scanning Probe Microscope Gratings for Moiré Interferometry," T.A. Winningham and K. Douglas, invention disclosure filed (July, 2001).

"Method for Utilizing Nanoscale Lithographic Masks to Pattern an Arbitrary Substrate via an Intermediate Transfer Layer," T.A. Winningham and K. Douglas, full utility patent application # 09/750,522 (January, 2001).

"Tunable Nanomasks for Pattern Transfer and Nanocluster Array Formation," T.A. Winningham and K. Douglas, full utility patent application #09/642,135 (August, 2000).

"Ordered Arrays of Nanoclusters," T.A. Winningham and K. Douglas, utility patent application #09/583,209 (May, 2000).