Nanometer-scale Science and Technology
Room: 304 - Session NS+HI-TuM

Nanopatterning and Nanolithography
Moderator: Nancy Burnham, Worcester Polytechnic Institute, Leonidas Ocola, Argonne National Laboratory

8:00am **NS+HI-TuM1 Nanoetching and Characterization Towards sub-5 nm Patterning**, ***Deirdre Olynick***, *D. Staaks, D. Tierno, S. Dallarto, S. Sassolini, B. Muddiman, Z. Lui, G. Calafiore*, Lawrence Berkeley National Laboratory, *X. Gu, T.P. Russell*, University of Massachusetts, Amherst, *M. Kocsis*, Inpria Corporation **INVITED**

Plasma etching is the ubiquitous method for high-resolution pattern transfer in semiconductor and related technologies. As lithographic techniques advance towards 5 nm half-pitch for applications in storage media, nanoelectronics, and plasmonic based devices, plasma etching processes must follow suit. This brings enormous and arguably insurmountable challenges using typical plasma hardware. For instance, very high etching selectivity must be achieved to accommodate mask heights (~1-2 times the feature size) which must shrink to mitigate pattern collapse in the lithographic and etching steps. In addition, line edge roughness at down to sub 1 nm levels must be achieved. To meet these enormous challenges we are investigating etching processes with temperatures down to -140 °C. Low temperature etching was first introduced by Tachi.[1] Lower etching temperatures can bring benefits such as higher selectivity processes, larger process windows, and reduced plasma damage which will be important for achieving sub-5 nm features.

We will discuss nanoscale cryogenic etching work in silicon, chromium, and silicon dioxide. With careful micron and deep nanoscale etching we show that cryogenic temperature etching of silicon, previously studied in great detail at the micron scale, [2,3] can provide extreme selectivity and anisotropy at the nanoscale even with soft masks derived from block copolymer lithography. Selectivity is enhanced while maintaining pattern verticality because resist etch rates decrease as temperature is lowered. Changing to a chromium hardmask increases selectivity towards deeper sub-10 nm features at 20:1 aspect ratios. Studies of chromium etching show a temperature dependent etch rate that can be used to enhance profile control and limit mask undercut, necessary when nanometer controlled is required. Finally, we will discuss investigations into reduced temperature silicon dioxide etching for applications in patterned media and vertical NAND.

References:

1. S. Tachi, K. Tsujimoto and S. Okudaira, Appl. Phys. Lett. (8), 616-618 (1988).

2. X. Mellhaoui, R. Dussart, T. Tillocher, P. Lefaucheux, P. Ranson, M. Boufnichel and L. J. Overzet, J. Appl. Phys. (10), 104901-104910 (2005).

3. J. Pereira, L. E. Pichon, R. Dussart, C. Cardinaud, C. Y. Duluard, E. H. Oubensaid, P. Lefaucheux, M. Boufnichel and P. Ranson, Appl. Phys. Lett. , 071501-071501-071503 (2009).

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8:40am **NS+HI-TuM3 Cut Patterning Challenges for the 14nm-Node and Beyond**, ***Ryan Jung***, *J.R. Sporre, F.L. Lie, S. Kanakasabapathy, S. Sieg*, IBM Albany Nanotech Center, *A. Ranjan, S. Voronin, A. Raley, V. Rastogi, A. Ko*, TEL Technology Center, America, LLC, *D. Lee*, Samsung Electronics

In order to satisfy certain device architecture, fabrication of certain levels such as channel and gate is typically done by first forming line and space arrays, followed by removing or cutting some lines or parts of lines to form the final pattern. For instance, the method of Sidewall Image Transfer (SIT) patterning generates pairs of lines that are structurally connected at the line ends. Accordingly, the line/space patterning must be supplemented with a companion cut mask pattern to remove these undesired features. The cut mask, in addition to removing undesired features, also facilitates orthogonal line end control and dense array tip-to-tip control, such as in memory device, that cannot be achieved solely from lithography side using mask optical proximity control (OPC) and negative tone developed resist. With channel and gate pitch being scaled down to below 80nm, the ability to precisely place the cut mask edge and to control the line end taper angle has a direct impact on defectivity and yield. The ability to control the critical dimension of the cut opening has a direct impact on the tip-to-tip CD and device density. This paper evaluates the advantages, technical challenges, and extendibility of various cut schemes for 14nm node and beyond, focusing on line edge profile and tip-to-tip control. This work was performed by the Research and Development Alliance Teams at various IBM Research and Development Facilities

9:00am **NS+HI-TuM4 Nanopore Memristors: Sub-10nm Devices Built on Membranes Milled with a Helium Ion Microscope**, ***Douglas Ohlberg***, *J.P. Strachan, W. Thompson, Z.Y. Li, R.S. Williams*, Hewlett Packard

A novel platform has been developed to fabricate and study the performance of memristive devices smaller than 10 nm. The platform consists of free-standing silicon nitride membranes into which holes or pores with diameters ranging in size from 7nm – 50 nm have been milled with a helium ion microscope. In addition to serving as a substrate, the membrane also acts as an interlayer dielectric, and devices are fabricated by sequential deposition of materials above and below the membrane to fill the nanopore. Since deposition of the layers does not require intervening exposures to resists, developer solutions, or plasma cleans, all interfaces are clean and free of contaminants that would otherwise degrade device operation. This approach enables the compositional engineering of ideal device stacks at the nanometer scale decoupled from the problems often introduced by conventional lithographies. Working memristors are demonstrated that have been successfully fabricated around nanopores with diameters as small as 7nm. In addition, we demonstrate, how the sidewall profiles of the nanopores can be engineered in a variety of shapes from conical to hour glass by the deposition, prior to helium ion milling, of materials on the membrane that influence the scattering dynamics of the ions during milling.

9:20am **NS+HI-TuM5 Characterization of Cluster-Based High-Resolution Inorganic Resists**, ***Rose Ruther***, *R.P. Oleksak, R. Frederick, B.T. Flynn, G.S. Herman*, Oregon State University

Both near- and long- term challenges for nanomanufacturing require significant advances in lithography to obtain sub-ten nanometer half-pitch. One approach to meet these challenges is through inorganic resists based on clusters and nanoparticles. Inorganic resists are of considerable interest due to the potential for both high resolution and low line width roughness (LWR), but generally suffer from low sensitivity. Recently, incorporation of radiation sensitive ligands into inorganic resists has enabled significantly improved sensitivity. For example, we have demonstrated the use of H_2O_2 as a radiation sensitive ligand for resists based on inorganic nano-clusters with the general formula, $Hf(OH)_{4-2x-2y}(O_2)_x(SO_4)_y{\cdot}qH_2O$ (HafSOx). By including H_2O_2 the HafSOx has significantly improved sensitivity to extreme UV photons and electrons, while still displaying high-resolution and low LWR.

In this presentation we characterize key steps in the lithographic process to gain insight into the nanodimensional patterning of HafSOx. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) confirm the presence of nanoscale particles in the precursor solutions. TEM is further used to characterize cross-sections of spin-coated HafSOx films before and after pattern exposure and development. Combined with energy dispersive X-ray spectroscopy (EDS) this allows for *in situ* investigations of the dynamic nature of both structural and compositional properties with electron exposure pertinent to the patterning process. In particular, oxygen species are found to be very mobile during TEM analysis and migrate to the Si interface with an associated densification of the HafSOx film. Cross-sectional TEM of patterned lines down to approximately 10 nm half-pitch provides unique information on pattern profiles and reveals the presence of inter-line residual material consisting of discrete structures consistent with solution species. Both temperature programmed desorption (TPD) and electron stimulated desorption (ESD) are used to characterize the key desorption species that occur during thermal and radiative processes during patterning. ESD indicates that the peroxo species have radiation sensitivity, where the primary desorption products are O_2 and H_2O. We find that the time evolution of the O_2 and H_2O desorption yields indicate much faster kinetics for O_2 desorption, suggesting that the formation of the insoluble oxide network is driven initially by desorption of peroxide groups as opposed to thermal dehydration. These data provide insight into the radiation-induced changes responsible for the contrast mechanism of this system.

9:40am **NS+HI-TuM6 Development Characteristics of PMMA in Alternative Alcohol:Water Mixtures**, ***Leonidas Ocola***, Argonne National Laboratory

In the past decade there has been a shift from toxic solvents used in lithography processing towards more environmentally safer chemicals. The most widely used resist in electron beam lithography is polymethylmethacrylate (PMMA). The standard developer is a solution mixture of isopropanol (IPA) and methyl isobutyl ketone (MIBK) in a ratio of 3:1. The Globally Harmonized System (GHS) Classification for MIBK includes the following entries: Flammable liquids (category 2), Acute toxicity, Oral (Category 5) and Inhalation (Category 4). The most popular environmentally friendly alternative is an IPA and water (H2O) solution in a ratio of 7:3. Excellent results have been published using this developer. The mechanism of why this solution works, given the fact that pure IPA and pure H2O do not develop exposed PMMA is not well understood. Furthermore, the IPA GHS Classification the following entry: Specific target organ toxicity - single exposure (Category 3), central nervous system. Our research is focusing on shedding light onto what would be the interaction of water with similar alcohols, such as methanol and ethanol, and environmentally safer alternatives to IPA. This turns out to be Ethanol. The only Ethanol GHS Classification entry is: Flammable liquids (Category 2). We find that ethanol water mixtures exhibit excellent contrast, sensitivity, and resolution, and should be considered as one of the most environmentally safe viable developer solution for PMMA. We will present results pertaining on our best lithography results using Ethanol:water solutions, and a possible explanation on the role of the water:alcohol interaction with the exposed PMMA resist. We do not believe it is just an issue of cosolvency but more of a localized molecular interaction. The goal of better understanding of this interaction is to help find safer developers for other resists that rely on solvent based development.

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11:00am **NS+HI-TuM10 Room Temperature Electron Beam Assisted Oxygen Purification of Electron Beam Induced Pt Deposits: Towards Pure and High-Fidelity Nanostructures**, ***Brett Lewis***, *M.G. Stanford*, University of Tennessee, *H. Plank*, Graz University of Technology, Austria, *J.H. Noh*, University of Tennessee, *J. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee

Electron Beam Induced Deposition (EBID) is a direct write mode capable of fabricating highly precise nanoscale structures by employing a scanning electron beam to disassociate adsorbed precursor molecules which subsequently condense on a substrate. The major drawback of the EBID process is that high purity metallic deposition is rarely achieved due to residual impurities attributed to the inadequate disassociation of the precursor molecule remaining in the final structure. Thus, purification strategies for nanoscale EBID deposits has been a critically important research area as EBID is poised to impact many nanoscale science and technology applications. To this end, our recent work has been focused on the post-deposition purification of EBID structures. We demonstrate a room temperature purification method in which platinum–carbon nanostructures deposited from $MeCpPtIVMe_3$ are purified by the presence of oxygen gas during a post-electron exposure treatment. Deposit thickness, oxygen pressure and oxygen temperature studies suggest that the dominant mechanism is the electron stimulated reaction of oxygen molecules adsorbed at the defective deposit surface. In this presentation we will overview the electron-stimulated reaction regimes as a function of oxygen partial pressure and temperature, and electron beam current and energy. We will overview electron stimulated reaction and adsorption/diffusive transport models to demonstrate that, for our experimental regime, we believe the rate-limiting mechanism is oxygen adsorption/transport. In addition to purification, the post-deposition electron stimulated oxygen purification process enhances the resolution of the EBID process due to the carbon removal of the as-deposited materials . Notably, pure platinum deposits with low resistivity and retain the original deposit fidelity were accomplished at room temperature.

11:20am **NS+HI-TuM11 Prospects for Nanofabrication using the Combination of STM-based Depassivation Lithography, Selective ALD, and Material Etch Processes**, ***Joshua Ballard***, Zyvex Labs, *S. Anz*, *S. Sando*, Systine, Inc., *M. Bischof*, University of North Texas, *D. Dick*, University of Texas at Dallas, *J. Fu*, National Institute of Standards and Technology (NIST), *D. Jaeger*, University of North Texas, *R. Longo*, University of Texas at Dallas, *J. Owen*, *E. Fuchs*, Zyvex Labs, *S. McDonnell*, University of Texas at Dallas, *R. Reidy*, University of North Texas, *Y.J. Chabal*, *R.M. Wallace*, University of Texas at Dallas, *J. Randall*, Zyvex Labs, *A. Cherala*, *S. Singhal*, *S. Sreenivasan*, University of Texas at Austin

Attaining the capability to produce top-down designed nanostructures at sizes and precisions at the nanometer and atomic scales will enable new classes of research into material and device behavior. First demonstrated in the mid-1990s, Scanning Tunneling Microscopy (STM) based hydrogen depassivation lithography has been shown to allow selective functionalization of surfaces with many types of molecules and materials with near absolute precision. Recently, selective Atomic Layer Deposition (ALD) of titania has also been demonstrated on such a functionalized surface, with the deposited material behaving as an etch mask in 3-D nanostructure formation. This results in a process that combines the high precision of STM with standard processing techniques to produce 3-D structures.

Already, 3-D structures with arbitrary shapes with full-pitches down to 13 nm have been fabricated using this process. This work will describe this process as well as provide an overview of the problems that need to be addressed to further reduce the minimum feature size and improve precision. Given the current and near term limitations of the process, classes of devices that have been and are possible to be fabricated will be described, including designed quantum dots, photonic structures, and NEMS apparatuses. Finally, pathways for scalability will be discussed.

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