

# Thursday Morning, October 22, 2015

## Nanometer-scale Science and Technology

Room: 212B - Session NS+MN-ThM

### Nanopatterning and Nanolithography/Nanoscale Mechanics

**Moderator:** Stephane Evoy, University of Alberta, Jeremy Robinson, Naval Research Laboratory

8:00am **NS+MN-ThM1 Electron Stimulated Desorption and Raman Investigations of HafSOx Inorganic Resists**, *Ryan Frederick, G. Herman*, Oregon State University

Hafnium oxide hydroxide sulfate (HafSOx) materials are under investigation as inorganic photoresists due to their high patterning fidelity, which is important for next-generation nano-lithography. In order to develop materials with better patterning sensitivity and higher resolution it is critical to understand the underlying mechanisms that result in the soluble/insoluble transition after exposure to radiation. Prior studies have shown that the incorporation of hydrogen peroxide into HafSOx is necessary to provide radiation sensitivity. In this presentation we will demonstrate that electron stimulated desorption (ESD) is a very useful technique for the characterization of radiation-induced mechanisms in HafSOx, and potentially other inorganic photoresists. These ESD studies are being performed with low energy electrons,  $E_{kin} = 50 - 500\text{eV}$ , which includes the range of photoemitted and secondary electron energies expected during extreme ultraviolet (EUV) lithography. In the case of HafSOx films we found significant  $\text{O}_2$  desorption during ESD for films containing hydrogen peroxide, and found no  $\text{O}_2$  desorption during ESD for films not containing hydrogen peroxide. These studies suggest that  $\text{O}_2$  is the primary ESD species, and this desorption product can be correlated with the radiation sensitive hydrogen peroxide that is incorporated in the HafSOx films. We have used the Menzel-Gomer-Redhead desorption model to determine the  $\text{O}_2$  ESD cross-sections over a range of electron energies and doses, and determined that the cross-sections range from  $2 \times 10^{-15}$  to  $8 \times 10^{-15} \text{cm}^2$ . To confirm that these low energy electrons can drive the soluble/insoluble transition in HafSOx we have measured contrast curves using ellipsometry to measure film thickness after exposing HafSOx to 100eV electrons for various electron doses and after development. The soluble/insoluble transition was found to occur in the electron dose range between 100 to 250  $\mu\text{C}/\text{cm}^2$ . We have also used Raman spectroscopy to better understand the radiation-induced processes in HafSOx by monitoring the metal coordinated peroxide species after various electron doses. There were very similar reaction kinetics when comparing the increase in  $\text{O}_2$  desorption signal during ESD and the decrease in the peroxide Raman signal for increasing electron dose. Finally, we will discuss the radiation-induced mechanisms in HafSOx and relate these to other inorganic photoresists being developed for EUV lithography.

8:20am **NS+MN-ThM2 Fundamental Limits of Material Toughening with Molecularly Confined Polymers**, *Scott Isaacson*, Stanford University, *K. Lioni, W. Volksen, T.P. Magbitang*, IBM Almaden Research Center, *R.H. Dauskardt*, Stanford University, *G. Dubois*, IBM Almaden Research Center

Low-density hybrid molecular materials with organic and inorganic components engineered at molecular length scales can be made to exhibit diverse mechanical, thermal, and optical properties. We present a novel class of hybrid nanocomposites created through a unique backfilling approach in which selected polymers are homogeneously infiltrated into the pores of a sol-gel nanoporous glass scaffold, leading to uniform mixing at unprecedentedly small length-scales ( $\sim 1 \text{nm}$ ) and confinement of polymer chains to dimensions far smaller than their bulk radius of gyration [1-3]. The second-phase material may be chosen from an extensive library of polymers, allowing for the development of composites with novel electrical, optical, and mechanical properties. This synthesis technique is versatile and can produce uniform, high-quality films over large areas.

We show that it is possible to dramatically improve the mechanical and fracture properties of a nanoporous organosilicate matrix by filling the porosity with a polymeric second phase. The degree of toughening is shown to increase with the polymer molecular weight, and is also found to depend on synthesis conditions. These studies of confined polymers enable us to explore the fundamental limits of nanocomposite toughening in terms of molecular strength, molecular size, and degree of confinement. We describe a novel toughening mechanism based on the molecular bridging and pullout of individual confined polymer chains from the porous matrix, distinct from the more common entanglement-based crazing mechanisms exhibited by bulk polymers. This mechanism is supported and quantified with a model

that describes the nanomechanical processes occurring on the length scale of individual polymer chains. The toughening model is further leveraged to calculate the tensile strength of individual polymer chains and find it in agreement with our own independent estimates of molecular strength. This study provides new insight into the mechanical behavior of polymer chains under nanoscale confinement and suggests potential routes for increasing the cohesive strength of multifunctional nanocomposites, where the traditional bulk toughening mechanisms may be absent.

[1] T. Frot, W. Volksen, S. Purushothaman, R. Bruce, G. Dubois, *Adv. Mater.* 2011, 23, 2828-32.

[2] T. Frot, W. Volksen, S. Purushothaman, R.L. Bruce, T. Magbitang, DC Miller, VR. Deline, G. Dubois, *Adv. Funct. Mater.* 2012, 22, 3043-3050.

[3] W. Volksen, K. Lioni, T. Magbitang, G. Dubois, *Scripta Mater.*, 2014, 74, 19-24.

8:40am **NS+MN-ThM3 Nanomanufacturing from Silicon to DNA**, *James Liddle*, Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899-6203

#### INVITED

The production of integrated circuits using silicon fabrication technology is the dominant nanofabrication technology in the world today. However, the industry is maturing, and the technology used for integrated circuit manufacturing, although extraordinarily impressive, is suited, economically, only for that function. At the same time, the nanotechnology revolution has delivered an array of novel structures and materials with fascinating and useful properties, but has presented us with several challenges. These include scaling up production and reducing costs to levels that are commercially interesting, and finding ways of integrating heterogeneous nanostructures into fully functional systems. I will illuminate these issues with a brief description of the strengths and weaknesses of the semiconductor manufacturing paradigm, a comparison with the possibilities offered by DNA-mediated assembly, and an illustration of how a deep understanding of nanoscale physics can turn optical metamaterials from a laboratory curiosity into a manufacturable product.

9:20am **NS+MN-ThM5 Pattern Formation by Ion Beam Sputtering on Thermally Treated Ge Surfaces Implanted with Si Ions**, *Angélica Guadalupe Hernández, Y. Kudriavtsev*, CINVESTAV-IPN, Mexico

We have investigated formation of patterned surfaces after low energy oxygen ( $\text{O}_2$ ) ion sputtering on germanium (Ge) crystals implanted with silicon (Si) ions and subsequent thermal annealing by using Atomic Force Microscopy (AFM).

A commercially available Ge crystal wafer was implanted with  $\text{Si}^+$  ions. The energy of implantation was 25 keV. This low energy and the high dose regime ( $2 \times 10^{16} \text{cm}^{-2}$ ) results a relatively high Si concentration obtaining at the implanted maximum of  $5.3 \times 10^{21} \text{atoms}/\text{cm}^3$ . Distribution and depth near-surface of implanted ions were calculated by Montecarlo simulations using TRIM software as 15 nm and confirmed by the Secondary Ion Mass Spectrometry (SIMS).

After ion sputtering a study of the surface morphology was performed by AFM for comparison of the obtained results with the Ge surface without implantation. In other hand, Raman spectra of the as implanted samples shows the vibration modes of  $\alpha$ -Ge, c-Ge, Ge-Si,  $\alpha$ -Si and Si-Si, which is an indicator of Si clusters formation in to the Ge bulk due to the ion implantation.

In order to recover the crystallinity of the Ge lattice, the thermal annealing at 700 °C during 5min under nitrogen ( $\text{N}_2$ ) atmosphere was performed. The corresponding Raman spectra shows the transition from amorphous to crystalline Ge.

After the thermal process, ion beam sputtering was performed by using  $\text{O}_2$  ions and energy beam of 0.5, 1 and 2 keV at different ion doses under ultra-high vacuum conditions (base pressure  $\sim 10^{-9}$  mbar). Due to the differences in the sputtering yield between Ge and Si, the preferential sputtering of Ge results in an enrichment of Si on the surface. The Si nano-crystals produces an effect of "shadow" leading to a formation of nano-structured surfaces. This results were compared with our previous work, where Ge surfaces (not implanted) were bombarded under the same sputtering conditions (ion specie, energy and ion dose).

Morphology of the surface was investigated by AFM of the original surface, as implanted samples, thermally treated and after ion bombardment. Finally, we compared the experimental morphology with ones obtained previously by the oxygen sputter Ge crystal.

9:40am **NS+MN-ThM6 Poor Q-factor? - No Problem: Nano-Optomechanical Mass Sensing in Ambient Conditions**, *Swapan Roy, V.T.K. Sauer, A. Venkatasubramanian, W.K. Hiebert*, University of Alberta and The National Institute for Nanotechnology, Canada

It has been demonstrated that optimum dynamic range (DR) and high quality factor (Q) of NEMS resonators provides unprecedented mass sensitivity [1]. The mass sensitivity and frequency stability of these devices are limited by their thermomechanical (TM) noise. TM noise goes down with Q as pressure increases, at the same time enhanced critical amplitude leads to a higher DR value with better sensitivity. However, detecting TM noise signal at ambient condition is always challenging. Optomechanical transduction successfully resolved this challenge with high displacement sensitivity and high bandwidth of NEMS devices [2]. Previously we have demonstrated robustness of our optical racetrack resonator transduction scheme in detecting TM noise signal [3]. Taking advantage of this measurement protocol we have found zeptogram level mass sensitivity at atmospheric pressure for a double clamped beam. This is similar to the sensitivity in high vacuum, even though Q-factor drops 300 fold from vacuum to ambient pressure. These intriguing experimental results challenge assumptions about fundamental limits of mass sensitivity of NEMS sensors and open the door for ultrasensitivity in ambient conditions.

1. K. L. Ekinci, Y. T. Tang and M.L. Roukes, "Ultimate limits to inertial mass sensing based upon nanoelectromechanical systems.", *J. Appl. Phys.* Vol. 95. No.5, March 2004.
2. M. Li, W. H. P. Pernice, C. Xiong, T. Baehr-Jones, M. Hochberg, and H. X. Tang, "Harnessing optical forces in integrated photonic circuits." *Nature*, Vol.456, pp.480-4, Nov.2008.
3. V. T. K. Saur, Z. Diao, M. R. Freeman, and W. K. Hiebert, "Optical racetrack resonator transduction of nanomechanical cantilevers." *Nanotechnology*, Vol.25, 05522, 2014.

11:00am **NS+MN-ThM10 Frequency Division Using a Micromechanical Resonance Cascade**, *K. Qalandar, M. Sharma, B. Gibson, Kimberly Turner*, University of California, Santa Barbara **INVITED**

A coupled micromechanical resonator array demonstrates the first successful realization of multi-stage frequency division. Frequency converters, dividers and multipliers, are necessary over a wide range of frequencies for a variety of applications, including vibration energy harvesters, RF transceivers, phase-locked loops, and quantum cascade lasers. In the VHF and UHF frequency range, solid-state and electromagnetic devices have traditionally dominated on-chip signal processing activities due to their wide bandwidth operation, programmability, and ease of implementation. However, design becomes more complicated and noise increases when cascading electronic dividers, due to buffers, amplifiers, and complex impedance matching circuits. Increasing constraints in size, power, and phase noise have led microelectromechanical systems (MEMS) to be considered in place of many traditional electronic elements. In particular, MEMS resonators are of interest since these high Q narrow bandwidth devices can provide better phase noise characteristics than similar devices that utilize amplifier technology. Coupled vibratory modes in micro-resonators have been shown to provide phase noise improvements in frequency sources, and have been considered in other contexts. This frequency divider combines the benefits of cascading, internal resonance, and mechanical coupling in a single micro-device. The operation is based on nonlinear dynamics and exploits the robustness of parametric resonance. This narrow-band approach uses a subharmonic resonance cascade in a chain of internally resonant subsystems with specific coupling that allows energy exchange between successive divide-by-two stages. The mechanical structure consists of a set of N sequentially perpendicular microbeams that are connected by relatively weak elastic elements such that the system vibration modes are localized to individual microbeams and have natural frequencies with ratios close to  $1 : 2 : \dots : 2N$ . Conservative (passive) nonlinear inter-modal coupling provides the required energy transfer between modes and is achieved by finite deformation kinematics. When the highest frequency beam is excited, this arrangement promotes a cascade of subharmonic resonances that achieve frequency division of  $2^j$  at microbeam  $j$  for  $j = 1; \dots; N$ . Results are shown for a capacitively driven three-stage divider in which an input signal of 824 kHz is passively divided through three modal stages, producing signals at 412 kHz, 206 kHz and 103 kHz. The system modes are characterized and used to delineate the range of AC input voltages and frequencies over which the cascade occurs. This narrow band frequency divider has simple design rules that are scalable to higher frequencies, and can be extended to a larger number of modal stages.

11:40am **NS+MN-ThM12 Single-Molecule Analysis with Nanomechanical Systems**, *Michael Roukes*, California Institute of Technology **INVITED**

Mechanical resonators based on NEMS (nanoelectromechanical systems) now enable measurement of the inertial mass of individual atoms and molecules [1]. We have employed NEMS to realize a new form of mass spectrometry (MS) with single molecule sensitivity, and have demonstrated the analysis of individual large-mass biomolecular complexes, one-by-one, in real-time [2]. In this talk I will survey progress and prospects in this emerging field. In particular, NEMS-MS offers transformational capabilities for the field of native MS, which focuses upon the topological investigation of intact protein complexes with high sensitivity and a theoretically unrestricted mass range. Recently, we have developed an approach that greatly enhances the capabilities of NEMS-MS by enabling imaging the spatial mass distribution of individual analytes – in real time, and with molecular-scale resolution – when they adsorb onto a NEMS resonator [3]. This new approach, which we term inertial imaging, employs the discrete, time-correlated perturbations induced by each single-molecule adsorption event to the ensemble of modal frequencies of a NEMS resonator. The spatial moments of each adsorbing analyte's mass distribution are deduced from the discrete, time-correlated shifts it induces to a multiplicity of vibrational modes. The lowest moment of the measured mass distribution function yields the total analyte mass; higher moments reveal the center-of-mass position of adsorption, the analyte's average diameter, and its spatial skew and kurtosis, etc. Together, these higher moments completely characterize the analyte's molecular shape. Once acquired, these moments can subsequently be inverted to yield an "inertial image" of each analyte. Unlike conventional imaging, the minimum analyte size detectable through nanomechanical inertial imaging is not limited by wavelength-dependent diffraction phenomena; instead frequency fluctuation processes determine the ultimate attainable resolution. Advanced NEMS devices are capable of resolving molecular-scale analytes.

- [1] Naik, A. K., Hanay, M. S., Hiebert, W. K., Feng, X. L. & Roukes, M. L., Towards Single-molecule Nanomechanical Mass Spectrometry. *Nature Nanotechnology* 4, 445–450 (2009).
- [2] Hanay, M. S., Kelber, S. I., Naik, A. K., Chi, D., Hentz, S., Bullard, E. C., Colinet, E., Duraffoug, L. & Roukes, M. L., Single-protein Nanomechanical Mass Spectrometry in Real Time. *Nature Nanotechnology*, 7, 602-608 (2012).
- [3] Hanay, M. S., Kelber, S. I., O'Connell, C. D., Mulvaney, P., Sader, J. E. & Roukes, M. L., Inertial Imaging with Nanomechanical Systems. *Nature Nanotechnology* 10, 339-344 (2015).

# Authors Index

**Bold page numbers indicate the presenter**

## — D —

Dauskardt, R.H.: NS+MN-ThM2, 1  
Dubois, G.: NS+MN-ThM2, 1

## — F —

Frederick, R.: NS+MN-ThM1, **1**

## — G —

Gibson, B.: NS+MN-ThM10, 2

## — H —

Herman, G.: NS+MN-ThM1, 1  
Hernández, A.G.: NS+MN-ThM5, **1**  
Hiebert, W.K.: NS+MN-ThM6, 2

## — I —

Isaacson, S.G.: NS+MN-ThM2, **1**

## — K —

Kudriavtsev, Y.: NS+MN-ThM5, 1

## — L —

Liddle, J.A.: NS+MN-ThM3, **1**  
Lionti, K.: NS+MN-ThM2, 1

## — M —

Magbitang, T.P.: NS+MN-ThM2, 1

## — Q —

Qalandar, K.: NS+MN-ThM10, 2

## — R —

Roukes, M.: NS+MN-ThM12, **2**  
Roy, S.K.: NS+MN-ThM6, **2**

## — S —

Sauer, V.T.K.: NS+MN-ThM6, 2  
Sharma, M.: NS+MN-ThM10, 2

## — T —

Turner, K.L.: NS+MN-ThM10, **2**

## — V —

Venkatasubramanian, A.: NS+MN-ThM6, 2  
Volkens, W.: NS+MN-ThM2, 1