

# Wednesday Morning, October 30, 2013

**Nanometer-scale Science and Technology**  
**Room: 203 B - Session NS+AS+BI+SP-WeM**

**Nanoscale Imaging and Microscopy**  
**Moderator: U.D. Schwarz, Yale University**

**8:00am NS+AS+BI+SP-WeM1 Outcomes of and Materials for Two University-Level Courses on Atomic Force Microscopy, N.A. Burnham, Worcester Polytechnic Institute**

The outcomes of and materials for undergraduate and graduate courses on atomic force microscopy (AFM) in the Physics Department at Worcester Polytechnic Institute are described [1]. Given since 2001, the courses have been well received by over 150 students – from freshmen to emeritus professors – 45% of whom go on to use their AFM skills in subsequent studies or professions. Over half of the enrollees have been students external to the author's home department. The course materials that have been developed are: YouTube videos [2], instrument lab instructions, computer lab instructions and programs, instructions and programs for labs with a macroscopically sized cantilever, classroom materials including writing exercises, and notes for teaching assistants and lecturers. Still under development is a textbook with homework problems. Most materials are available upon request from the author in order to promote AFM courses at other institutions, with the intent to draw more students into the intriguing world of nanoscience.

1. Accepted for publication in *J. Nano Education*
2. <http://www.youtube.com/user/AtomicForceMicro/featured>

**8:20am NS+AS+BI+SP-WeM2 Imaging Li and B in a Glass Sample with 100nm Lateral Resolution Using NanoSIMS, Z. Zhu, Pacific Northwest National Laboratory, Y. Wang, University of Florida, J. Crum, Pacific Northwest National Laboratory, Z. Wang, Chinese Academy of Science**

A widely used method to immobilize nuclear wastes is fusing them into glasses. These proposed glass waste forms are multicomponent complex material with the common components of Li and B compounds. During the fast cooling process, phase separation occurs in the form of 200-500 nm clusters and the glass matrix. It is difficult for commonly-used surface analysis tools (e.g., X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, scanning electron microscope/energy dispersive spectroscopy (SEM/EDX), and transmission electron microscope/energy dispersive spectroscopy (TEM/EDX)) to characterize the distributions of ultra-light elements like Li and B in these two phases. For example, although TEM/EDX characterization can show mapping of heavy elements in the two phases, this technique is not ideal to identify the location of ultra-light elements, such as Li and B, because the sensitivity of EDX analysis for Li and B is poor. NanoSIMS can provide nano-scale spatial resolution (down to 50 nm) as well as excellent sensitivity for Li and B, making it a good candidate to image Li and B in the glass sample. We have used NanoSIMS to map Li and B in the glass sample with a lateral resolution of  $\leq 100$  nm. NanoSIMS images clearly show enrichment of both Li and B in the matrix phase.

**8:40am NS+AS+BI+SP-WeM3 Visualization of Subsurface Features in Soft Matrix using Atomic Force Microscopy Techniques, K. Kimura, K. Kobayashi, H. Yamada, Kyoto University, Japan**

Imaging of deeply buried subsurface features in soft matrices such as parasites in red blood cells [1], carbon nanoparticles in living cells [2], and buried electronic circuit in industrial products [3] have been demonstrated by heterodyne force microscopy [4] (HFM). Subsurface imaging using ultrasonic AFM (UAFM), which is a technique to evaluate contact stiffness with high sensitivity, has also been demonstrated in some papers. However, UAFM has been mainly applied for imaging subsurface features in hard matrices such as Si and metals, whose resolved maximum depth was typically less than 200 nm [5]. In this study, we visualized Au nanoparticles buried in a polymer matrix under 960 nm from the surface by using HFM and UAFM, which has never been achieved [6].

A dispersion of Au particles (50-nm-diameter) was dropped on a polyimide sheet (125-micro-meter-thick). After drying, a top-coat (photo polymer) was spin-coated on it and annealed at 150°C. Top-coat thickness was estimated from the film coated on a Si wafer. We used a modified commercial AFM instrument (JEOL: JSPM 4200). The sample was directly glued on a piezoelectric plate, which was fixed on a tube scanner. Another piezoelectric plate for HFM was attached on a cantilever holder. The contact resonance frequency used for imaging was determined by

measuring the thermal noise spectrum of the cantilever contacted on the sample. The schematic diagrams of HFM and UAFM are shown in Figs. 1 and 2 in the supplemental file.

We performed subsurface imaging for the samples with the top-coat thickness of up to 1 micro-meter. We found that the maximum depth of the subsurface features resolved by HFM and UAFM depends on the spring constant ( $k$ ) of the cantilever. Figure 3 in the supplemental file shows subsurface images of Au particles buried under a top-coat of 900-nm-thick obtained by UAFM using a Si cantilever ( $k$ : 1.3 N/m), which we found the most suitable for subsurface imaging on the polymer matrix. We suppose that subsurface features in a soft matrix at least buried under 1 micro-meter from the surface affect surface viscoelasticity, which are detected by AFM techniques when a cantilever of suitable stiffness is used.

This work was supported by the Murata Science Foundation and Grant-in-Aids from the Japan Society for the Promotion of Science (JSPS).

- [1] G. S. Shekhawat et al., *Science* **310** (2005) 89.
- [2] L. Tetard et al., *Nature Nanotech.* **3** (2008) 501.
- [3] S. Hu et al., *J. Appl. Phys.* **109** (2011) 084324.
- [4] M. T. Cuberes et al., *J. Phys. D* **33** (2000) 2347.
- [5] Z. Parlak et al., *J. Appl. Phys.* **103** (2008) 114910.
- [6] K. Kimura et al., *Ultramicroscopy* (2013) in press (10.1016/j.ultramicro.2013.04.003).

**9:00am NS+AS+BI+SP-WeM4 Nanoscale Characterization Using Resonance Enhanced Infrared Spectroscopy, E. Dillon, M. Lo, C. Prater, K. Kjoller, Anasys Instruments, M. Belkin, F. Lu, University of Texas at Austin**

As current research focuses on shrinking the size of devices and the components that comprise these devices, the characterization of these systems becomes more and more challenging. The resolution of conventional IR spectroscopy techniques is diffraction limited to a practical resolution limit of  $\sim 3$   $\mu\text{m}$ . This length scale is too large to observe any potential nanoscale features on today's devices. Atomic force microscopy (AFM) is a widely used nanoscale imaging technique that provides the user with a high spatial resolution topographic map of a sample surface. When combined, the resulting AFM-IR can provide the high resolution topographic maps commonly associated with AFM with the addition of high spatial resolution IR spectroscopy and IR imaging. Currently, AFM-IR spectroscopy has the ability to collect IR spectroscopic information below the diffraction limit with a lateral resolution of  $\sim 100$  nm. However, there are still some limitations that prevent its use on many important nanoscale systems. One of the main limitations is the thickness of sample required for examination ( $> 100$  nm). Overcoming these limitations has a dramatic impact by enabling widespread use of nanoscale IR spectroscopy for spatially resolved chemical characterization. The use of a quantum cascade laser (QCL) as the IR source significantly increases the sensitivity of AFM-IR. The QCL has repetition rates 1000 times higher than previous lasers used for AFM-IR. This allows the ability to pulse the laser at the resonant frequency of the AFM cantilever giving rise to a high IR sensitivity mode referred to as resonance enhanced infrared nanospectroscopy (REINS). Due to the increased IR sensitivity, less laser power is required to generate a spectrum, meaning samples that were too thin or easily damaged using previous AFM-IR techniques can now be easily examined. Using REINS we have been able to collect nanoscale IR spectra and perform chemical imaging on films as thin as 10 nm. These advances in AFM-IR allow for the characterization of samples from a wide variety of applications, including, organic photovoltaic materials, materials for energy generation and storage, cellular biology, development of advanced polymeric materials and integrated circuit devices.

**9:20am NS+AS+BI+SP-WeM5 AFM-based Chemical and Mechanical Property Characterization of Low-k/Cu Interconnects, M. Lo, Anasys Instruments, S.W. King, Intel Corporation, E. Dillon, Q. Hu, R. Shetty, C. Prater, Anasys Instruments**

Infrared (IR) spectroscopy is a powerful technique for characterizing the chemical bonding in low dielectric constant (i.e. low-k) materials utilized in nano-electronic Cu interconnect structures. Combined with nanoindentation and other techniques, IR spectroscopy has enabled the structure-property relationships in these materials to be determined. However, such property analysis have been primarily limited to characterizing blanket films due to the spatial resolution of a typical IR measurements being diffraction limited to ca. 3 - 10  $\mu\text{m}$ . Further advances in low-k materials and failure analysis would be greatly enhanced by the ability to perform IR spectroscopy and other material property characterization on actual nanometer scale low-k/Cu interconnects. In this report, we demonstrate both AFM based IR chemical

analysis and contact resonance mechanical analysis of a single layer 90 nm low-k/Cu interconnect structure.

To achieve better spatial resolution in IR spectroscopy measurements, a broadly tunable infrared laser was coupled to an atomic force microscope (AFM-IR). IR laser pulses at the wavelengths of the low-k materials characteristics absorption bands was utilized to create rapid thermal expansion that invoked vibrations in the AFM tip directly in contact with the sample. Amplitudes of the ringing motion of the AFM tip were recorded as the same tip scanned over the areas of interest. By detecting only the perturbations directly underneath the AFM tip, spatial resolution below the diffraction limits of IR radiation could therefore be achieved. In this manner, IR spectra and 2D images of a < 1.5  $\mu\text{m}$  wide interlayer dielectric (ILD) in a low-k/Cu interconnect were achieved.

To complement the AFM-IR technique and achieve nanometer scale structure property measurements, AFM-based contact resonance (CR-AFM) measurements were performed in parallel. The CR-AFM technique probes the relative mechanical property of different materials and has been previously demonstrated useful for characterizing the elastic properties of low-k material in similar Cu interconnect structures. For the current CR-AFM measurements, the resonant frequency of the AFM tip was controlled by modulating the alternating current going through a specialized ThermoLever™, which interacts with the magnetic field of a magnet nearby. As this tip scans from ILD to other metallic layers, the frequency of the AFM tip vibration changes due to the variations in the mechanical stiffness from one material to another. By combining the AFM-IR and CR-AFM techniques, both chemical and mechanical analysis of a low-k/Cu nano-electronic structure were achieved using an AFM at high spatial resolution.

9:40am **NS+AS+BI+SP-WeM6 Amino Acid Immobilization and Surface Diffusion of Copper**, *E. Iski*, University of Tulsa, *A.J. Mannix*, *B.T. Kiraly*, *M.C. Hersam*, Northwestern University, *N.P. Guisinger*, Argonne National Laboratory

The 2D-scale study of relevant biomolecules, like amino acids, is pertinent for a variety of applications from the origin of biological homochirality and the amplification of surface chirality to the examination of noncovalent supramolecular interactions. Importantly, the study of these molecules on a copper surface may also be significant to the medical community as the binding of amino acids/proteins to copper ions plays a major role in the development of neurodegenerative diseases, like Mad Cow's Disease and Alzheimer's. The need for pristine molecular resolution of these systems requires the use of ultra-high vacuum scanning tunneling microscopy (UHV STM) as the primary technique for these studies. Through the detailed examination of the self-assembly behavior of five amino acid molecules on a Cu(111) single crystal, a fascinating and unexpected phenomenon was discovered. All of the amino acids assisted in the immobilization of copper atoms on the surface. The energetic landscape of the surface as mediated by temperature and molecular coverage facilitated the growth of copper islands and clusters. The growth and size fluctuation of the islands offered an interesting snapshot of metal nanocluster diffusion that often occurs at time scales beyond the resolution of a given surface science technique. The presence of  $\sim 1$  ML of molecules on the surface effectively trapped the metal atoms into localized islands. Elevated temperatures ( $\leq 350$  K) were used to promote further diffusion, coalescence, and extinction of the islands for a more detailed understanding of the coarsening and ripening mechanisms. In conclusion, while these systems provide insights into the chiral assembly of amino acids on Cu(111), they also provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms, which is important for the understanding of thin film growth and its morphological evolution.

10:40am **NS+AS+BI+SP-WeM9 Catalytic Model Systems Studied by High-Resolution, Video-Rate Scanning Tunneling Microscopy**, *F. Besenbacher*, Aarhus University, Denmark, *J. Kibsgaard*, Stanford University

For decades single-crystal surfaces have been studied under ultra-high vacuum (UHV) conditions as model systems for elementary surface processes. This "surface science approach" has contributed substantially to our understanding of the processes involved in especially catalysis.

In this talk I will show how STM can reveal fundamental processes in relation to catalysis, and how we can extract quantitative information on surface diffusion of adatoms and molecules. We use time-resolved, high-resolution STM images/movies to understand diffusion of vacancies, interstitials and molecules, e.g. water molecules on oxide surfaces, sintering and diffusion of nanoclusters on oxide surfaces, diffusion of intermediate species, and to identify active sites and to determine new nanostructures with novel catalytic properties (see [www.phys.au.dk/spm](http://www.phys.au.dk/spm)). The atomic-scale information obtained may even lead to the design of new and improved catalysts in certain cases.

11:20am **NS+AS+BI+SP-WeM11 Scanned Probe Based**

**Nanofabrication on Silicon: Progress, Challenges and Technology Spin-Offs**, *J.W. Lyding*\*, University of Illinois at Urbana Champaign **INVITED**

Atomic-scale nanofabrication on Si(100) surfaces can be achieved by using hydrogen as an atomic layer electron resist. Electrons from a STM probe can create atomically precise patterns of clean silicon under ultrahigh vacuum conditions. These patterns can serve as templates for selective chemistry, including the atomically precise placement of molecules on the silicon surface. By performing these studies under UHV conditions it is also possible to obtain information about the hydrogen desorption process. Two desorption regimes are observed. The first involves the direct excitation of the bonding-to-antibonding transition and requires an electron energy of  $\sim 6.5$  eV. In this regime a constant quantum desorption efficiency is observed irrespective of the electron current. At electron energies insufficient to excite the direct bonding-to-antibonding transition, desorption also occurs but with a strong current-dependent desorption efficiency. In this regime, the STM electrons inelastically excite the Si-H vibrational modes, which have a long lifetime of  $\sim 10$  ns. Thus, if the excitation rate, which depends on the electron current, exceeds the quenching rate by the lattice, then the Si-H bond moves up its vibrational state ladder until desorption occurs from the hot ground state. Atomic resolution patterning is a side benefit of this vibrational heating process since tunneling electron energies are involved. Following a suggestion by Avouris, these experiments were extended to deuterated Si(100) surfaces where a giant kinetic isotope effect was observed. In the single-particle desorption regime, when excitation to the antibonding level occurs deuterium accelerates more slowly away from the silicon surface, thereby enhancing the probability that the bond will reform. Experimentally, deuterium is observed to be about two orders of magnitude more difficult to desorb than hydrogen. In the vibrational heating regime the deuterium desorption probability decreases by many orders of magnitude due to the short Si-D vibrational lifetime ( $< 1$  ns). The STM isotope experiments set the stage for the discovery that deuterium can be used to dramatically reduce hot carrier degradation in silicon CMOS technology. Hot carriers at the transistor gate dielectric-silicon interface desorb the hydrogen used to passivate silicon dangling bonds. Deuterating the interface increases chip hot carrier lifetimes by more than an order of magnitude. Consequently, deuterium processing is now used in advanced chip manufacture. We have also developed a novel tip sharpening method for STM and AFM probes that results in sub-5 nm radii probe tips with ultra-hard conductive coatings.

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\* NSTD Recognition Award

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Belkin, M.: NS+AS+BI+SP-WeM4, 1  
Besenbacher, F.: NS+AS+BI+SP-WeM9, 2  
Burnham, N.A.: NS+AS+BI+SP-WeM1, **1**

## — C —

Crum, J.: NS+AS+BI+SP-WeM2, 1

## — D —

Dillon, E.: NS+AS+BI+SP-WeM4, **1**;  
NS+AS+BI+SP-WeM5, 1

## — G —

Guisinger, N.P.: NS+AS+BI+SP-WeM6, 2

## — H —

Hersam, M.C.: NS+AS+BI+SP-WeM6, 2  
Hu, Q.: NS+AS+BI+SP-WeM5, 1

## — I —

Iski, E.: NS+AS+BI+SP-WeM6, 2

## — K —

Kibsgaard, J.: NS+AS+BI+SP-WeM9, **2**  
Kimura, K.: NS+AS+BI+SP-WeM3, **1**  
King, S.W.: NS+AS+BI+SP-WeM5, 1  
Kiraly, B.T.: NS+AS+BI+SP-WeM6, 2  
Kjoller, K.: NS+AS+BI+SP-WeM4, 1  
Kobayashi, K.: NS+AS+BI+SP-WeM3, 1

## — L —

Lo, M.: NS+AS+BI+SP-WeM4, 1;  
NS+AS+BI+SP-WeM5, **1**  
Lu, F.: NS+AS+BI+SP-WeM4, 1  
Lyding, J.W.: NS+AS+BI+SP-WeM11, **2**

## — M —

Mannix, A.J.: NS+AS+BI+SP-WeM6, **2**

## — P —

Prater, C.: NS+AS+BI+SP-WeM4, 1;  
NS+AS+BI+SP-WeM5, 1

## — S —

Shetty, R.: NS+AS+BI+SP-WeM5, 1

## — W —

Wang, Y.: NS+AS+BI+SP-WeM2, 1  
Wang, Z.: NS+AS+BI+SP-WeM2, 1

## — Y —

Yamada, H.: NS+AS+BI+SP-WeM3, 1

## — Z —

Zhu, Z.: NS+AS+BI+SP-WeM2, **1**