

SYMPOSIUM NN

Scanning Probe Microscopy in Materials Research

November 28 - December 1, 2005

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* Invited paper

8:30 AM *NN1.1

Nano-Technology of Polymers for Local Probe Data Storage Applications. Urs Duerig¹, Bernd Gotsmann¹, Armin Knoll¹, Thomas Altbauer¹ and Johannes Windeln^{2,1}; ¹IBM Research GmbH, Rueschlikon, Switzerland; ²IBM Deutschland GmbH, Mainz, Germany.

Ultrahigh storage areal densities can be achieved by using thermo-mechanical local-probe techniques to write, read back, and erase data in the form of nanometer-scale indentations in thin polymer films. Thermal and mechanical robustness, long term bit retention, low mechanical stress writing conditions, and repeated erasability of written indents are the essential criteria for a polymer storage medium. Based on extensive research we can reconcile these criteria in terms of generic physical material properties: Glass transition temperature, cross link density, and yield activation energy. By cross linking the polymer chains, an elastic matrix is generated which performs two functions: (1) It assists erasure of written indents by providing a restoring pressure for the recovery of the polymer surface into its flat state. (2) The polymer chains are locally anchored which prevents the formation of surface ripples during repetitive reading of the data in an AFM imaging mode. The glass transition acts as a thermal switch between a hard, glassy state at low temperature and a soft, deformable state at elevated temperature of the polymer. Bits are written in the soft state and the deformed meta-stable state is stabilized in the hard, glassy state. We have carefully studied the dynamics of bit writing in the hot state and the relaxation dynamics in the cold state. The kinetics of bit writing is governed by the well-known WLF time-temperature relation, which we have tested on nanometer and microsecond scales. Relaxation of the indents is governed by thermally activated events with an energy barrier that depends on the local bit stress. We have shown that all basic requirements for a storage media, viz. fast bit writing, repeated erase/overwriting of the same bit, greater than 10 year bit retention time, can be achieved with suitably engineered polymers. Most strikingly, we have also shown that polymers offer unprecedented storage density potential under realistic operating conditions in the multi Tbit/in² range which makes them the ideal media choice for local probe storage applications.

9:00 AM NN1.2

SPM Patterning of Nanoscale Metal-Molecule-Metal Junctions. James Batteas¹, Jayne Garno² and Christopher Zangmeister³; ¹Department of Chemistry, Texas A&M University, College Station, Texas; ²Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana; ³NIST, Gaithersburg, Maryland.

The ability to precisely construct nanoscopic metal-molecule-metal junctions is of great importance for the development of molecule based electronic and optoelectronic devices. Several methodologies to construct such junctions have been presented in recent years including fabrication with break-junctions, molecular lithography, cross bars, metal nanoparticle contacts, nanotransfer printing, nanoimprint lithography, nanopores and template grown nanowires. Scanned probe lithography (SPL) offers the capability for patterning surface features with nanoscopic dimensions. Moreover, the ability of SPL to generate structures of variable sizes affords the construction of a range of complex architectures. Electroless deposition of metals has previously been applied as a practical approach for the controlled deposition of metal onto surfaces. By combining SPL with electroless metal deposition, metal-molecule-metal junctions can be constructed where the dimensions and surface organization are dictated by the placement of surface groups active for electroless deposition, such as carboxylates, into a desired pattern. Herein we report the patterning of nanosized metal-molecule-metal junctions, specifically Cu on carboxylic acid terminated SAMs on Au, using a combination of automated AFM-based nanofabrication and electroless metal deposition. The architecture of the Cu nanostructures are tunable in all dimensions by controlling the written 2-D pattern size of the fabricated structures, the surface density of reactive acid groups, and the concentration of reactants in the electroless plating solution.

9:15 AM NN1.3

Nanopatterning Functionalization of Diamond Surfaces. Claudio Manfredotti^{1,2} and Chiara Manfredotti^{1,2}; ¹Experimental Physics, University of Torino, Torino, Italy; ²NIS Center of Excellence, Torino, Italy.

Diamond surfaces can be functionalized by hydrogenation and oxidation: while hydrogenated surfaces are hydrophobic, oxidized ones are hydrophilic. These modified surfaces can be used for a

selective adsorption of polar species in a wide range of pH values, for a new kind of alkanes (with hydrogenated surfaces) and of alkenes (with oxidized surfaces) chemistry, for electrochemical applications (diamond has the widest potential window), for selective DNA attachment, etc. Moreover, considering that the hydrogenated diamond surface is perfectly transparent and electrically conducting, it can be used both for recording electrical signals from cells and for their electrical stimulation, together with an optical monitoring by a confocal microscopy, even in time-consuming experiments, since the percentage of survivals is relatively large. Local Anodic Oxidation (LAO) of hydrogenated CVD diamond surfaces by a conducting AFM has been introduced as one of the best ways for selective nanopatterning of surfaces and for their subsequent visualization but, in order to be suitably exploited, this technique has to be checked with respect to precision and reproducibility. In this work, LAO over epitaxial CVD diamond surfaces has been carefully investigated as a function of the scanning speed, relative humidity and bias voltage. As examples, a perfect control of the width of the oxidized lines between 80 and 110 nm has been demonstrated for scanning speeds between 20 and 110 nm/s, at 60% relative humidity and between 45 and 90 nm by switching the humidity from 40% to 60%. The oxidation process is indicated by the decay of the current during LAO process, which is terminated in about 10 s. The interpretation of the results, which could oscillate between digging grooves and creation of oxidized bumps, is still quite difficult, since it depends on the AFM mode ("contact" or "non contact") which has been used for LAO. The obtained results together with their interpretation and possible developments will be presented and discussed.

9:30 AM NN1.4

Nano-size Phase Change Random Access Memory Cell Fabricated by Femtosecond Laser Direct Writing Assisted with Near-field Scanning Optical Microscopy. Weijie Wang^{1,2}, L. P. Shi¹, R. Zhao¹, H. K. Lee¹, P. K. Tan¹, X. S. Miao¹, Y. Lin², Y. H. Wu^{1,2} and T. C. Chong^{1,2}; ¹Data Storage Institute, Singapore, Singapore; ²Department of Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore.

Data storage industry is now searching high performance nonvolatile memory (NVM) technology for stand alone memory, portable electronics and embedded applications. Phase Change Random Access Memory (PCRAM) is considered as one of the best candidates to compete with the charge storage Flash memory. Since the energy required for phase transformation decreases with PCRAM cell size, the write current scales down with the cell size. This unique high scalability advantage of PCRAM distinguishes it from other emerging NVM technologies. The memory nanocells were fabricated by the femtosecond laser direct writing assisted with near-field scanning optical microscopy (NSOL) in order to overcome the optical diffraction limitation of the conventional optical lithography. The assembled NSOL system combined with stepper technology has been used to construct PCRAM device structure with a specially designed fabrication process. The nanocell features were opened on the dielectric layer with cell feature size varying from 800 nm down to less than 100 nm, toward 45 nm. The phase change material with a sandwich structure was sputtered as the recording layer. The nanocell functional performances were tested by a home-built tester, and the scalability of the programming current as a function of the memory cell features was investigated. RESET current (R-I curve) of 0.8mA was observed with a short pulse width 70 ns for the memory nanocell at feature size of 90 nm. The results presented a low current and fast switching of the phase change material change from crystalline state (lower resistance) to amorphous state (high resistance).

9:45 AM NN1.5

Local Resistive Memory Switching in NiO Thin Films. Jung Bin Yun¹, Hyunjung Shin¹, David H. Seo², Sunae Seo², Myoung-Jae Lee², Seung-Eon Ahn², In-Kyeoung Yoo² and Dong-Chul Kim²; ¹School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; ²Devices Lab, Samsung Advanced Institute of Tech, Yongin, South Korea.

In recent, many researchers have been studied various materials such as chalcogenide alloys (Ge₂Sb₂Te₅), conducting polymers, doped perovskite SrZrO₃, and perovskite PCMO (Pr_{0.7}Ca_{0.3}MnO₃) as a candidate for next generation non-volatile memory. Among them, transition metal oxides for example, NiO, Nb₂O₅, and TiO₂ etc., are now attractive much attention due to their processing compatibility with Si, superior device scalability as well as chemical stability. (We deposited Pt/NiO(100nm)/Pt/Ti on SiO₂/Si by dc magnetron sputtering and measured I-V (current-voltage) to verify switching behavior. By voltage sweep with compliance of 1mA, current value abruptly increased two orders of magnitude at about 5V (forming) and NiO layer changed from higher resistance state to lower resistance one. While sweeping again, current value decreased two orders of magnitude at close to 1V. By the next voltage sweep, current value abruptly increased at close to 2V less than the forming voltage.

Voltage repeated sweeps were done to confirm bi-stable memory switching behavior between the high & low resistance states. We used conducting Atomic Force Microscopy (C-AFM) to study the switching characteristics of oxide thin films. Utilizing C-AFM, we were able to directly observe nano-sized filamentary current paths contribute to switching through NiO thin films. By applying a suitable voltage or current, nano-sized filamentary current paths can be switched to two resistance states which can be utilized for resistance based memory on the nanometer scale. Fluctuated current values through each filament led to voltage and current distribution. Our results establish that switching in oxides is due to nano-sized filamentary current paths of 20-45 nm and that the size of these paths could be able to scale down for high density of memory cell. Also, by controlling of these filaments, we could be able to reduce voltage distribution for operation of devices and programming current. Several researchers have investigated the mechanisms behind the memory switching in transition metal oxides. In this study, C-AFM allows us to propose the mechanism for the memory switching event in NiO and provide much concrete physical model for the devices.

SESSION NN2: Studying Surfaces with Noncontact
AFM and STM
Chair: Suzi Jarvis
Monday Morning, November 28, 2005
Back Bay C (Sheraton)

10:30 AM NN2.1

Study of Reconstructions on SrTiO₃ (100) Surfaces by Noncontact Atomic Force Microscopy and Kelvin Probe Microscopy. Rui Shao and Dawn A. Bonnell; Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

SrTiO₃ surfaces have received great attentions because of its relevance to catalysis, thin film growth and electronic devices. Knowledge of the nature of reconstructions on SrTiO₃ surfaces is critical to their applications. In this work, several surface reconstructions: c(2x2), 2x2, c(6x2), (r5xr5)R26.6 and (r13xr13)R33.7 were prepared and characterized with scanning tunneling microscopy (STM), noncontact atomic force microscopy (ncAFM) with atomic resolution, as well as electron diffraction. Several atomic models were evaluated based on our experimental results. We find strong evidence that c(2x2), 2x2 prepared in reducing atmosphere are due to oxygen vacancies, and (r5xr5)R26.6 and (r13xr13)R33.7 are due to Sr adatoms. We demonstrate that ncAFM gives higher resolution on c(6x2) than STM. The model and the imaging mechanism on this surface are presented. Frequency-modulated Kelvin Probe Microscopy was used to characterize different electronic properties of these reconstructions.

10:45 AM NN2.2

Atomically resolved NC-AFM imaging on group-IIa fluoride/Si(111). Yoshihide Seino, Shota Yoshikawa, Masayuki Abe and Seizo Morita; Graduate school of Engineering, Osaka University, Suita, Osaka, Japan.

Non-contact Atomic Force Microscopy (NC-AFM) is the unique experimental method which is capable of imaging non-conducting surfaces with atomic resolution. Until now, chemical resolution of different species at surfaces of binary compounds, such as NaCl, KBr, MgO, Al₂O₃, and CaF₂, remains one of the main challenges for NC-AFM. In these cases, the image contrast qualitatively depends on the sign of charge and/or spatial distribution of the electrostatic potential produced by the tip apex structure and/or composition. The chemical identity of atomic features observed on surfaces still remains unclear, mainly due to the uncertainty in the structure and chemical composition of tips. We have mainly investigated the surface structure of CaF₂/Si (111) on atomic scale for clarifying the contribution of the electrostatic potential between the tip and the surface atom species using NC-AFM operated at room temperature in ultrahigh vacuum environment. According to our NC-AFM experiments, the topographic images were classified into two patterns, one was obtained to use the tip apex characterized with the positive electrostatic potential and the other was with negative one. According to a line profile of topographic images, the atom positions of topmost three layers in CaF₂ film surface could be recognized clearly as one Ca ion and two F ions, and the results was consistent with the result of (111) cleaved surface and the NC-AFM simulations. The topographic images, moreover, have been obtained by carefully controlling the distance between tip and the surface. By use of our advanced experimental techniques, higher atomic resolution has been achieved in comparison with the other proceeding results obtained as the topographic images in our NC-AFM system. Such the capability of high spatial resolution has led to the chemical identification on the ionic surfaces by applying the mixed ionic system, for instance, of Ca_xSr_{1-x}F₂/Si (111). The image conditions of mixed ionic surfaces will become clear in more detail, it will be advanced into the techniques of atomic manipulation or atomic

assembling on insulator surfaces.

11:00 AM *NN2.3

Mechanical Atom Manipulation and Artificial Nanostructuring at Room Temperature based on Noncontact-AFM Method. Seizo Morita^{1,2}, Yoshiaki Sugimoto¹, Noriaki Oyabu¹, Oscar Custance² and Masayuki Abe^{1,2}; ¹Department of Electrical Electronic and Information Engineering, Osaka University, Suita, Osaka, Japan; ²Handai FRC, Suita, Japan.

Recently we created "Atom Inlay" -embedded atom letter "Sn" - that was comprised of substitutional 19 Sn atoms embedded in Ge(111)-c(2x8) reconstructed surface [1]. This novel artificial nanostructuring using mechanical atom manipulation method has several significant differences from conventional ones as follows: (1) "AFM" that can be applicable even to insulating materials was used instead of STM. (2) "Selective Atom Manipulation" that selectively manipulated two kinds of atom species such as intermixed Sn and Ge atoms was used instead of conventional atom/molecule manipulation method. (3) "Atom Interchange Lateral Manipulation" phenomenon that can interchange two kinds of different atom species such as adjacent Sn and Ge atoms was discovered and used for creating nanostructure. (4) "Atom Inlay" -embedded atom letter "Sn" - that is a novel artificial nanostructure was created at room temperature (RT). This novel artificial nanostructuring method may enable us to search and create complex nanomaterials and nanodevices with novel functions consisted of many atom species even on insulating substrate at RT. In this review talk, we will introduce how to discriminate different atom species, how to induce atom interchange lateral manipulation, and how to create artificial nanostructure such as embedded atom letter "Sn" [1]. References [1] Y. Sugimoto, M. Abe, S. Hirayama, N. Oyabu, O. Custance and S. Morita; "Atom inlays performed at room temperature using atomic force microscopy", Nature Materials, Vol.4, Issue 2 (2005) pp.156-159.

11:30 AM NN2.4

Scanning Tunneling Microscopy Investigations of Surface Dynamics to Determine Step Edge Diffusion Barriers.

Jennifer Y. Lee¹, Chris A. Pearson² and Joanna Mirecki Millunchick¹; ¹Materials Science & Engineering, University of Michigan, Ann Arbor, Michigan; ²Physics, University of Michigan, Flint, Michigan.

Investigating the growth of strained alloy films has been a long-standing problem in surface science. Models of strained film growth based on elastic strain energy predict unique morphologies for different strain: islands upon large terraces for compressive films and mesas separated by trenches for tensile films. We have used a combined MBE-STM system to image 2 ML thick films both in compression (InAs or GaSb) and in tension (GaAs or AlAs) grown on InP(001) at a range of temperatures and also with different growth fluxes of group III material. A roughness analysis reveals that the skewness of the height distribution for InAs is positive, which is indicative of a morphology dominated by islands, while for AlAs the skewness is negative, which is indicative of a morphology dominated by holes. These results agree with the previously described morphologies predicted using elastic strain energy considerations. The Ga containing compounds also follow this strain energy trend, except the terraces or mesas have significantly rougher steps and higher surface anisotropies. These observations suggest that in addition to the sign of the misfit strain, factors such as step edge diffusion contribute to surface roughness. From an analysis of the images we compute the step edge density (step edge length per unit area) versus deposition flux and use a recent level set model [1] to extract values of step edge diffusion. These results may explain the morphology observed in short period superlattice structures that exhibit lateral composition modulation. [1] C. Ratsch, J. Garcia, and R. E. Caflisch, submitted to Applied Physics Letters.

11:45 AM NN2.5

Self-Organized Growth of Nanopucks on Pb Quantum Islands. Ya-Ping Chiu¹, Hsin-Yu Lin^{1,2}, Tsu-Yi Fu³, Chia-Seng Chang¹ and Tien-Tzou Tsong¹; ¹Institute of Physics, Academia Sinica, Taipei, Taiwan; ²Department of Chemical Engineering, National Central University, Chungli, Taiwan; ³Department of Physics, National Taiwan Normal University, Taipei, Taiwan.

Electronic Moire patterns found on lead (Pb) quantum islands can serve as a template to grow self-organized cluster (nanopucks) arrays of various materials. These patterns can be divided into fcc- and hcp-stacked areas, which exhibit different binding strengths to the deposited adatoms. For Ag adatoms, the binding energy can differ substantially and the confined nucleation thus occurs in the fcc sites. Both the size distribution and spatial arrangement of the Ag nanopucks are analyzed and found to be commensurate with the characteristics of the template island, which exhibits a bi-layer oscillatory behavior. In this presentation, we will also discuss the electronic properties of these Ag nanopucks with emphasis upon their

dependence on size and shape.

SESSION NN3: Latest Developments in Scanning Probe Techniques

Chairs: Urs Duerig and Hirofumi Yamada
Monday Afternoon, November 28, 2005
Back Bay C (Sheraton)

1:30 PM NN3.1

High-Resolution Imaging and Chemical Characterization of Heterogeneous Materials with the Confocal Raman-AFM. Ute Schmidt, Matthias Kress, Klaus Weishaupt and Olaf Hollricher; WITec GmbH, Ulm, Germany.

A thorough knowledge of structural and chemical properties is essential for the fields of nanotechnology and materials science, leading to a growing demand for characterization methods for heterogeneous systems on the nanometer scale. However, certain properties are difficult to study with conventional characterization techniques due to either limited resolution or the inability to chemically differentiate materials without inflicting damage or using invasive techniques such as staining. The Confocal Raman AFM combines Raman spectroscopy, a chemical analysis technique, with high-resolution imaging methods such as Confocal Microscopy and Atomic Force Microscopy (AFM). With this instrument it is possible to analyze heterogeneous materials with respect to their chemical composition and surface structure without laborious sample preparation. The materials can be analyzed under ambient conditions or in a liquid environment. With the Confocal Raman Microscope (CRM), it is possible to obtain Raman spectra from extremely small sample volumes and to collect high resolution Raman images. In the Raman spectral imaging mode, a complete Raman spectrum is acquired at every image pixel and the images are extracted by analyzing spectral features (sum, peak position, peak width, etc.). By simply rotating the microscope turret, the CRM is transformed into an Atomic Force Microscope (AFM). With this technique, a sharp tip is scanned over the sample, providing high resolution topographical images with sub-nanometer resolution. By investigating the tip-sample interaction, one can obtain not only the high resolution topographic structure of the surface but also information about the local mechanical properties of the sample components. The highly resolved topographic structures observed with the AFM can then be linked to the chemical information obtained by the CRM. To demonstrate the capabilities of this unique combination of measuring techniques, examples from various fields of application such as biology, polymer, and semiconductor physics will be shown.

1:45 PM NN3.2

Ultramicrotome SPM - a Tool for 3D Reconstruction of Polymer Internal Structures. Anton Efimov and Sergei Saunin; NT-MDT Co., Moscow, Russian Federation.

Scanning probe microscopy (SPM) methods enable to study surface topography and local physical properties with spatial resolution of about 10 nm. However currently abilities of SPMs are limited by analysis of surface structures only and do not allow the investigation of the bulk properties and morphology. In recent time great interest came up for methods combining the abilities of SPMs with possibility of 3-D structure analysis. In this work we will discuss existing tomography methods based on investigation of thin sections of the objects and instrumentation aspects of their combination with Scanning Probe Microscopy as well as some sample preparation. Thin sections of polymer materials could be obtained with ultramicrotomes. However the procedure of preparation and consequence analysis of sections by means of electron microscopy is rather complicated and time-consuming. Sections obtained by ultramicrotome are often not so useful for SPM investigation as well. The structure of ultrathin(10-50 nm) sections is usually distorted by compression and knife so 3D reconstruction of SPM images becomes complicated. Contrary to electron microscopy SPM is able to investigate not only sections but also the surface of the blockface after sectioning, which shows less section artifacts [1]. This allows the acquisition of series of SPM images of the object after consequent sections. To enable in-situ SPM measurements of blockface surface a specialized SPM measuring head based on NT-MDT NTegra SPM compatible with Leica Microsystems UC6 ultramicrotome was designed and fabricated. 3D reconstructions of two-phase polymer nanocomposite structures based on series of consequent SPM images is presented as an example. Presented results show that the proposed technique opens a new approach to polymer and nanocomposite structure analysis by 3D nanotomography with a resolution of tens of nm. [1] N. Matsko and M. Mueller, AFM of biological material embedded in epoxy resin, Journal of Structural Biology, Vol. 146, 3, p. 334 (2004).

2:00 PM *NN3.3

Single Spin Detection Using Magnetic Resonance Force Microscopy. Raffi Budakian^{1,2}, D. Rugar² and H. J. Mamin²; ¹Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²IBM Almaden Research Center, San Jose, California.

Magnetic resonance force microscopy (MRFM) is an emerging technique for direct nondestructive three-dimensional imaging with potential applications to imaging of individual molecules, buried interfaces, nanostructures and inhomogeneous solids. MRFM combines ultrasensitive force detection and magnetic resonance to manipulate and detect sub-surface electron or nuclear spins with high sensitivity and spatial resolution. Recently, we have used MRFM to image a single electron spin with 25 nm lateral resolution located as deep as 100 nm below the surface of a silica sample containing a low concentration of silicon dangling bonds. A key advance that has made this result possible has been the development of a novel spin manipulation protocol that allows us to detect the statistical imbalance in small spin ensembles. In addition to the detection of single electron spin, we have used this technique to follow the statistical fluctuations in a small ensemble of spins and apply real-time feedback to control the time evolution of the spin orientation. Through the use of feedback, we have demonstrated that spins can be hyperpolarized or "cooled" in the rotating frame of the measurement, transferred and stored in the lab frame and later read out. With modest improvement to the current detection signal-to-noise ratio, this technique could be used to initialize and readout the quantum state of a single electron spin in real-time.

3:30 PM NN3.4

Video Rate Atomic Force Microscopy. Andrew David Laver Humphris¹, David J. Catto¹, Cvetelin Vasilev² and Jamie K. Hobbs²; ¹Infinitema Ltd, Oxford, United Kingdom; ²Department of Chemistry, University of Sheffield, Sheffield, United Kingdom.

Scanning probe microscopy (SPM) offers unique imaging capabilities as it is able to provide nanometre resolution in air, liquid and vacuum environments, with no pre-treatment or coating of the sample. This has led to the very widespread use of SPM ranging from basic research in biology and material science through to industrial applications such as quality assessment and inspection. However, unlike far field imaging methods that collect data in a parallel fashion, due to the scanning nature of SPM, it is necessary for the image to be collected one pixel at a time, line by line in series, thus severely limiting the rate at which an image can be obtained. Typically, a conventional atomic force microscope (AFM) will take from 10 seconds to a few minutes to acquire an image. This severely limits the microscopes ability to follow processes at the molecular level, which often occur on the millisecond time scale due to the relaxation time of the molecules, and prevents large area inspection. Other applications that are limited by the low image acquisition rates include data storage and nanolithography. In this paper the limitations of conventional approaches to SPM will be considered and new methods that overcome these problems will be introduced. A video rate AFM will be presented that utilises a novel feedback system and micro resonant scanner [1]. The video rate AFM is capable of collecting images of a 3 micron x 3 micron area in less than 40 milliseconds, which is approximately 1000 times faster than conventional methods. To achieve this, the microscope operates with a tip velocity in excess of 20 cm per second compared to 20 microns per second in a conventional AFM. High speed dedicated hardware has been developed and enables the images to be collected and displayed to the operator in real time. The ability of the video rate AFM to follow processes at the molecular level with millisecond time resolution has been demonstrated by observing polymer processes such as crystallisation of a molten polymer surface and results will be presented. The high frame rate of the microscope also reduces the effect of the external environment and enables the user to explore the surface of the sample with nanometre resolution in real time. Large areas can be mapped with nanometre resolution by tiling individual high speed images. We believe that the presented video rate AFM demonstrates the step like improvement that SPM requires if these techniques are to deliver the capabilities sought by the advancing fields of biotechnology and nanotechnology. [1] A.D.L. Humphris, M.J. Miles and J.K. Hobbs, Appl. Phys. Lett., 034106 (2005).

3:45 PM *NN3.5

Development and Trial Measurement of Synchrotron-Radiation-Light Illuminated Scanning Tunneling Microscope. Taichi Okuda¹, Toyooki Eguchi¹, Kotone Akiyama¹, Masanori Ono¹, Masayuki Hamada¹, Takeshi Matsushima¹, Ayumi Harasawa¹, Akira Kataoka¹, Toshi An¹, Yukio Hasegawa¹ and Toyohiko Kinoshita²; ¹Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, Japan; ²Japan Synchrotron Radiation Research Center, SPring-8, Mikazuki, Hyogo, Japan.

Towards realizing an element specific & atomic-resolution

spectro-microscopy, we are developing the synchrotron-radiation-light illuminated scanning tunneling microscope (SR-STM) [1,2]. Combining the SR light and STM, we can excite the element specific core electrons and detect the photocurrent together with the tunneling current by an STM-tip. This may enable us to make an element specific STM observation. Although it may be difficult to achieve the atomic resolution within the present technique (i.e., limit of the brilliance of the current SR source), we have tried to obtain the X-ray absorption spectra from very small area by the STM tip as a first step. We connected the originally designed STM system to the undulator beamlines (BL13C & 19A) at the Photon Factory, Tsukuba, Japan. The monochromated soft-X-ray light was impinged at the grazing incidence (4°) and the photoexcited current was detected by an STM tip. Samples such as Au/Si(111) surface, mesoscopic Ni dots fabricated onto Si wafer etc. are prepared for checking the performance of the apparatus. We successfully observe the soft-X-ray absorption spectra around Ni *M* & *L*, Si *L*, and Au *N* edges by the tip. The detection area seemed to be approximately $10\text{--}100\mu\text{m}^2$ order. This poor resolution may be caused by the large detection area of the photoexcited current by the tip. In order to improve the spatial resolution, namely to reduce detecting photocurrent by a side-wall of an STM-tip, we have coated the side wall of the tip by polyethylene glycols. The detection current could be reduced by this procedure; however, the sample surface was contaminated easily. Therefore instead of such polymers, a glass-coated tungsten tip whose bare apex is less than $5\mu\text{m}^2$ in length is fabricated [3]. This tip seemed to work well for the present purpose. Further, to detect a very small photo-excited current by a tip, the modulation technique is applied by chopping the SR light (1 kHz). The present status of the study and some trial techniques will be introduced. [1] T. Matsushima et al., Rev. Sci. Instrum. 75, 2149 (2004). [2] T. Okuda et al., J. Electron Spectrosc. Relat. Phenom. 144-147, 1157 (2005). [3] K. Akiyama et al., Rev. Sci. Instrum., to be published.

4:15 PM NN3.6

X-TIP: Joining X-Ray spectroscopies to Local Probe

Analysis: a new tool for nanoscience. Olivier Dhez¹, Comin Fabio², Roberto Felici¹, Chevier Joel³, Francesco Rocca⁴, Mario Rodrigues^{2,3}, Daniela Besana¹, Daniel Pailharey⁵, Juris Purans⁶ and Vaino Sammelselg⁷; ¹OGG/INFN/CNRS, Grenoble, France; ²ESRF, Grenoble, France; ³LEPES, UJF/CNRS, Grenoble, France; ⁴IFN/CNR, Trento, Italy; ⁵CRMC-N, CNRS, Marseille, France; ⁶IISP, Riga, Latvia; ⁷UNITA, Tartu, Estonia.

Local probe Microscopies are leading actors in the nanotechnology development areas. They provide key functionalities like provision of surface morphology, manipulation and modification of nanosamples, local characterisation of a number of physical properties. They provide then a detail insight on a local scale that can go down to the atomic scale. The radiation provided by installations like the ESRF, can, on the other end, provide a much deeper insight on the chemical characteristic of the sample by being able to determine chemical composition, chemical state, bond lengths and dynamical properties of atomic species at surface, but presents important limitations in lateral resolution due to intrinsic diffraction limit of X-ray optics. On top, the possibility of "touching, feeling and mechanically interacting" with samples of nanometric dimension is a feature that synchrotron radiation does not have despite its importance as characterization tool in the nanoworld. We have then two ranges of techniques that provide complementary possibilities and specificities and it appears extremely tempting to merge them in order to get a deeper understanding of physical and chemical properties in nanoscience. X-Tip is and EU STREP FP6 project aimed to provide instrumentation for merging Synchrotron Radiation and local probe techniques in a unique characterisation tool. The program involves different work-packages that deal with the different possibilities: SNOM detection of low energy photons, electron detection of photoemitted atoms, capacitance measurements and mechanical interaction with surfaces. The contribution aims to present the possibilities, limitations, actual advance and first results of the project.

4:30 PM NN3.7

Quantitative Probe Dynamics for Electromechanical Scanning Probe Microscopy. Stephen Jesse, Arthur P. Baddorf and Sergei V. Kalinin; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Piezoresponse Force Microscopy (PFM) and Atomic Force Acoustic Microscopy (AFAM) are nanoscale probes of local electromechanical and mechanical properties, including Young modulus, piezoelectric response, and recently, orientational imaging of ferroelectric and piezoelectric materials. Previous work has demonstrated that PFM and AFAM are highly effective tools for biological imaging since most bio-materials possess a measurable degree of piezoelectrical activity and elastic modulus variation between dissimilar components. The variations in the degree, ordering, and orientation of the response throughout the sample are indicative of functional variations within

the material. To fully understand and properly interpret PFM and AFAM generated images, it is critical to understand the mechanisms of signal transduction of the cantilever induced surface oscillations. The fragile nature of many bio-materials necessitates the use of relatively soft cantilevers with spring constants on the order of 0.1 nN/m. However, the pliability of these cantilevers leave them much more susceptible to spurious effects that are not directly related to the electromechanics of the substrate. These include local electrostatic interactions at the tip-surface junction and long range electrostatic effects between the cantilever and the surface. In addition, dynamic behavior is further complicated since imaging is often performed at the first and higher order resonances to improve the signal to noise ratio. Here, we present a detailed analysis of probe dynamics using a combination of modeling and experimentation. We are able to differentiate the contributions of extraneous effects from the true piezo response experimentally by varying the tip bias conditions over a range of AC frequencies and DC offsets, providing 2D spectroscopy of probe dynamics. The frequency dispersion of the nulling bias, the DC bias at which the measured response to AC excitation becomes zero, yields a measure of electrostatic vs. electromechanical contributions. Frequency-bias spectral measurements were carried out for vertical and two orthogonal lateral displacement conditions, providing information for the proper interpretation of vector PFM. The differences between transduction mechanisms for vertical and in-plane response components are analyzed. It is shown that lateral PFM imaging is optimal at low frequencies, while vertical PFM is best at high frequencies where dynamic stiffening reduces the electrostatic and longitudinal electromechanical contributions in the signal. The resonances are related only by the elastic properties of material, allowing simultaneous AFAM and PFM imaging using a frequency tracking approach. Several examples of imaging of biological and inorganic systems using simultaneous AFAM and PFM detection are illustrated. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

4:45 PM NN3.8

Single Electron Manipulation and Spectroscopy by Force Detected vacuum tunneling to individual Electronic States.

C. C. Williams and E. Bussmann, Department of Physics, University of Utah, Salt Lake City, Utah.

A new scanning probe imaging and spectroscopic technique, based upon the detection of single electron tunneling events by electrostatic force, has been developed. Single electrons are manipulated to and from individual electron states in a non-conducting surface by this method. This manipulation is achieved by adjusting the applied probe Fermi energy (voltage) above and below the energy of the electronic state at the surface. The tuning of the voltage also provides a method to determine the energy of the electron state. In these measurements, telegraph noise is sometimes observed at specific voltages, as the probe Fermi-energy passes through the energy of the state. The new nanometer scale approach provides the means to locate and identify electronic states in non-conducting surfaces, opening for exploration a whole class of materials and structures not accessible to the STM. The technique will be described and the manipulation and spectroscopic results will be presented.

SESSION NN4/L6: Joint Session: Scanning Probe Techniques

Chair: James Batteas

Tuesday Morning, November 29, 2005

Back Bay C (Sheraton)

8:00 AM NN4.1/L6.1

Assembly and Nanomechanics of Collagen Type II.

Henrik Birkedal^{1,4}, Sailong Xu^{2,4}, Mathias H. Bunger^{3,4}, Mingdong Dong^{2,4} and Flemming Besenbacher^{2,4}; ¹Department of Chemistry, University of Aarhus, Aarhus, Denmark; ²Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark; ³Department of Endocrinology and Metabolism C, Aarhus University Hospital, Aarhus, Denmark; ⁴Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Aarhus, Denmark.

Collagen type II is the main part of the organic matrix of cartilage and the growth plate found in vertebrates. The latter is the locus of bone growth in the developing child and critical for normal bone development. From a mechanical point of view, the growth plate is particularly interesting because it can be expected to be a 'soft' tissue in a 'hard' environment and it should thus be subjected to extra mechanical stress. Indeed, fractures in children are often found to occur at the growth plate. Motivated by a wish to understand these tissues at a molecular scale, we studied the self assembly of collagen type II and the nanomechanical properties of the resulting fibrils using atomic force microscopy (AFM) and force microscopy. Human collagen type II was assembled in simulated body fluid (SBF) for varying

lengths of time. Under acidic conditions, pH 4-5, no fiber formation was observed. However, at pH 8.5 fibers formed, which at later times further assembled into fibrillar assemblies. We studied the mechanical properties of these fibrillar assemblies on a mica surface in SBF buffer by force spectroscopy in the AFM. Analysis of the single molecule events showed an average rupture force on the order of 0.3 nN. Comparison with the results of similar experiments on collagen type I reveals that collagen type II has a longer extension length than type I.

8:15 AM NN4.2/L6.2

Study of Mechanics of Human Epithelial Cells During Ageing and its Possible Treatment: AFM Study In-Vitro. Igor Sokolov, S. Iyer and C. D. Woodworth; Physics and Chemistry Departments, Clarkson University, Potsdam, New York.

Goal of the study: Study mechanics of ageing epithelial cells and its possible biochemical alteration. Methodology: We used atomic force microscopy (AFM) with a probe modified by 5- micron sphere. Such a modification was done to minimize a possible harm to cell during the measurements, and to be able to measure rather soft areas of the cell, which were not measured before. Results: We found that the epithelial cells have three distinctive regions of different rigidity: the nucleus, cytoplasm, and edge areas. We measured rigidity of young cells (10 to 20 population doublings) and old cells (over 40-60 doublings) that were near senescence. We found that the Young's modulus of viable cells was consistently increased 2- to 10-fold in older versus younger cells. We also found that the increased rigidity of ageing cells was due to a higher density of cytoskeletal fibres, mostly microfilaments, F-actin, as we showed by using both immunofluorescence and a novel AFM-based technique. Using drugs that inhibit polymerization of F-actin, we managed to recover the rigidities of old viable cells back to the young level in all three areas of rigidity simultaneously. Conclusions: These results may contribute to a treatment of the age-related loss of elasticity in epithelial tissues.

8:30 AM NN4.3/L6.3

Electromechanical and Elasticity Imaging of Human Teeth by Scanning Probe Microscopy. Brian J. Rodriguez¹, S. Habelitz², I. Ivanov³, S. V. Kalinin³ and A. Gruverman⁴; ¹Physics, North Carolina State University, Raleigh, North Carolina; ²Preventative and Restorative Dental Sciences, University of California, San Francisco, California; ³Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ⁴Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Coupling between electrical and mechanical behavior is a universal feature of biological systems. Many biosystems, including teeth, are composed of dissimilar structural elements arranged in a complex hierarchical structure spanning multiple length scales down to the nanometer scale. Therefore, reliable methods for structural and electromechanical imaging on the nanoscale are required to understand the biological functionality of these materials. As a result of recent advances in nanoindentation and scanning probe microscopy (SPM), micro- to nanoscopic studies of the mechanical and electromechanical properties can now be performed. Here, we report a scanning probe microscopy (SPM) approach for electromechanical imaging of organic components in calcified matrix of dental tissues based on the detection of the local piezoelectric response. Electromechanical imaging by means of Piezoresponse Force Microscopy (PFM) shows a clear difference between dentin and enamel regions due to the different fractions of piezoelectrically active protein components. Direct evidence on the presence of 100-nm size protein inclusions in enamel in a deciduous human tooth is reported. Ultrasonic Force Microscopy (UFM) has been used in conjunction with PFM for simultaneous elastic imaging of dental tissues. Pure collagen has been also characterized by PFM as a reference sample. The enamel region exhibits no detectable piezoelectricity, and is found to be more rigid than the soft dentin, consistent with the hydroxyapatite structure of the enamel and the piezoelectric collagen in the dentin. In addition, nanoscale imaging of protein structure by PFM is correlated with micro-Raman measurements, providing information on local tooth structure and its chemical composition. The future opportunities of electromechanical SPM for characterization of complex biological systems are discussed. Research partially performed as a Eugene P. Wigner Fellow (SVK) at ORNL, managed by UT-Battelle, LLC under DOE contract DCE-AC05-00OR22725. AG acknowledges financial support of the National Science Foundation (Grant No. DMR02-35632).

8:45 AM NN4.4/L6.4

Nanoscale Intermolecular Forces of Bovine Tibial Cortical Bone of Varying Mineral Content. Kuangshin Tai and Christine Ortiz; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nanoscale intermolecular forces that exist in the extracellular matrix of bone expect to play significant roles in determining morphology (e.g. via apatite precipitation, collagen-hydroxyapatite interactions), structural integrity, interaction with bone fluid and constituent biomolecular species, as well as synthetic bone implant materials. The powerful technique of high resolution force spectroscopy (HRFS), which employs a nanosized probe tip at the end of a soft microfabricated cantilever force transducer, was used to directly measure piconewton-level surface forces that exist on samples of adult bovine tibial cortical bone as a function of probe-tip sample separation distance (henceforth referred to as "distance"). Samples were cut longitudinally from the tibial metaphysis, polished to a 0.05 μ m finish, and progressively demineralized with 40 H3PO4. Mineral content ranged between 3-57 weight (wt.%)%, measured by back-scattered electron microscopy, depending on the etch time. HRFS was carried out using a 3-D Molecular Force Probe (Asylum Research) at a displacement rate of 1 m/s in aqueous solutions with ionic strengths (IS) of 0.001-1M NaCl (pH 5.5). An Au coated V-shaped Thermomicroscopes cantilever probe tip (k = 0.042N/m, R(tip) = 85nm) was functionalized with HS-(CH2)10-COOH (carboxy terminated self-assembling monolayer or COOH-SAM). HRFS data on "approach" (i.e. probe tip advancing towards surface) for the bone surface showed a nonlinearly increasing net repulsive force for D > 5nm and frequent jump-to-contacts for D < 5nm. The Hamaker constant ("A") was determined from both jump-to-contact distances and power law fits at high salt concentrations (1M), where electrostatic forces are largely screened out. Both methods were consistent and showed that "A" increased with increasing mineral content (A4wt.% = A17wt.% = 30 zJ, A32wt.% = 50 zJ, and A57wt.% = 150 zJ). Using these values, HRFS data on approach at 0.01M was fit to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory yielding; 4wt.% = -0.005C/m², 17wt.% = -0.0026C/m², 32wt.% = -0.0075C/m², 57wt.% = -0.015C/m². On "retract" (i.e. probe tip moving away from the surface), long-range, nonlinear attractive events were frequently observed for partially demineralized samples. For 4wt.%, the average max attractive Force/R(tip) was 12.4 \pm 7.7mN/m, 7.7 \pm 4.1mN/m, and 11.0 \pm 4.6mN/m for 0.001-0.1M IS, respectively (statistically significant differences, p<0.01). Detachment distances were 182 \pm 111nm, 194 \pm 141 nm, and 209 \pm 100 nm (statistically insignificant differences for 0.001-0.01M IS comparisons, p>0.1 but significant for others, p<0.001), which is on the order of the contour length of individual collagen molecules. Pull-off events were rarely observed (<5%) for undemineralized bone (57 wt.%) but were very frequent (90%) for the 4 wt.% sample. These results will be discussed in light of zeta potential measurements on bone and compared to bioactive bone implant materials.

9:00 AM *NN4.5/L6.5

Atomic Structure and Dynamics of Membrane Proteins Revealed by Microscopy. Dimitrios Fotiadis, Patrick Frederix and Andreas Engel; M. E. Mueller Institute, Biozentrum, University of Basel, Basel, Switzerland.

Membrane proteins are membrane-embedded nanomachines that fulfill key functions such as energy conversion, solute transport, secretion, and signal transduction. To observe such processes and understand them at atomic level, purified membrane proteins are reconstituted in the presence of lipids. The latter restore the native environment and allow structure and function of membrane proteins to be assessed. Electron microscopy provides 3-D information at atomic resolution, and atomic force microscopy (AFM) surface structure and dynamics of membranes at sub-nm resolution. In addition, AFM is the method of choice to study the conformation and molecular arrangements of proteins in native membranes. We have developed sample preparation methods and optimized the imaging conditions that warrant high resolution to be obtained routinely as illustrated by a wide variety of membrane proteins (AQP0, AQP1, AqpZ, bacteriorhodopsin, connexins, light harvesting complexes, rhodopsin)^{1,2,3,4,5}. Recently, we have introduced electrically insulated conductive tips mounted on a cantilever for use in an AFM and operated in liquid. These probes are microfabricated and designed for measurements on biological samples in buffer solution, but they can also be employed for electrochemical applications, in particular scanning electrochemical microscopy. Variations of less than 1 pA in faradaic current were measured with a lateral resolution of 7.8 nm on the hexagonally packed intermediate layer of *Deinococcus radiodurans*⁶. 1. Engel, A. & Mueller, D. J. (2000). Observing single biomolecules at work with the atomic force microscope. *NatStructBiol* 7, 715-8. 2. Fotiadis, D., Hasler, L., Mueller, D. J., Stahlberg, H., Kistler, J. & Engel, A. (2000). Surface tongue-and-groove contours on lens MIP facilitate cell-to-cell adherence. *JMolBiol* 300, 779-89. 3. Fotiadis, D., Liang, Y., Filipek, S., Saperstein, D. A., Engel, A. & Palczewski, K. (2003). Atomic-force microscopy: Rhodopsin dimers in native disc membranes. *Nature* 421, 127 4. Mueller, D. J., Hand, G. M., Engel, A. & Sosinsky, G. E. (2002). Conformational changes in surface structures of isolated connexin 26 gap junctions. *EmboJ* 21, 3598-607. 5. Oesterhelt, F., Oesterhelt, D., Pfeiffer, M., Engel, A., Gaub, H. E.

& Mueller, D. J. (2000). Unfolding pathways of individual bacteriorhodopsins. *Science* 288, 143-6. 6. Frederix, P., Gullo, M., Akiyama, T., Tonin, A., de Rooij, N., Staufer, U. & Engel, A. (2005). Assessment of insulated conductive cantilevers for biology and electrochemistry. *Nanotechnology* 16, 997-1005.

9:30 AM NN4.6/L6.6

Polypeptide-Solvent Interactions Measured by Single Molecule Force Spectroscopy. Alexei A. Valiaev^{1,4}, Dong-Woo Lim², Ashutosh Chilkoti^{2,4}, Scott Schindler³ and Stefan Zauscher^{1,4}; ¹Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina; ²Department of Biomedical Engineering, Duke University, Durham, North Carolina; ³Institute of Statistics and Decision Sciences, Duke University, Durham, North Carolina; ⁴Center for Biologically Inspired Materials and Materials Systems, Duke University, Durham, North Carolina.

Stimulus-responsive biomacromolecules attract large research interest due to their potential applications in areas such as drug delivery, molecular motors and nanoscale devices. Here we report on our experiments on elastin-like polypeptides (ELPs) using single molecule force spectroscopy (SMFS) by AFM. ELPs are stimulus-responsive polypeptides that undergo the inverse phase transition and contain repeats of the five amino acids Val-Pro-Gly-Xaa-Gly (VPGXG), where Xaa is a guest residue. We show that SMFS can be used to quantify the effect of a guest residue, pH and ionic strength on molecular conformation of the polypeptide. The observed force-extension behavior at intermediate and large extensions supports a phenomenological model that describes ELPs as kinetically mobile, disordered macromolecules. Elasticity upon extension arises both from a deformation of the polypeptide backbone and from hydrophobic polymer-solvent interactions. Using SMFS we were able to differentiate the force-extension of ELP constructs synthesized with different guest residues, and we argue that these differences arise from differences in the hydrophobic hydration of side chains that ensue when the molecule is mechanically stretched. Our results are supported by recent MD simulations that suggest that hydrophobic hydration of side-chains plays an important role for ELP elasticity and provides the molecular basis for the inverse temperature transition behavior.

9:45 AM NN4.7/L6.7

Measuring Micromechanical Properties in Biological Attachment Devices. Steffen Orso, Ulrike G. K. Wegst, Christoph Eberl and Eduard Arzt; Max-Planck-Institute for Metals Research, Stuttgart, Germany.

A precise and detailed characterisation of biological structures and their mechanical properties is required, if engineers and designers wish to model and emulate the principles of their mechanical function and the optimisation found in them. While a number of methods exist to determine microstructure and geometry of biological samples, the mechanical characterisation of many of the structures that currently are of particular interest to researchers is still difficult due to their size and arrangement. One example for this are devices for 'dry' and reversible adhesion found in the attachment systems on the feet of insects and geckos. They consist of thousands of setae of several tens to 100 micrometers in length and a few micrometers in diameter and thus their mechanical characterisation is challenging. A novel method allows the micromechanical testing in bending, tension and compression of samples of a few tens of micrometers in length and a few micrometers or less in diameter. It uses a focussed ion beam (FIB) system as an *in situ* laboratory for sample preparation, fixation and testing. Advantages of this method are that samples from larger objects can be prepared site-specifically using the FIB, and that testing in tension is possible without end effects due to gripping, since the samples are affixed by metal 'tapes' deposited using the FIB. Forces are measured with a piezoresistive atomic force microscope (AFM) tip attached to a micromanipulator for high precision positioning. The displacement is determined from FIB micrographs taken during the test. For the first time, the strength and Young's modulus of an individual seta of the hairy attachment systems of the beetle *Gastrophysaviridula* could be determined using this method.

SESSION NN5: Scanning Probe Applications in Biology
Chair: Suzi Jarvis
Tuesday Morning, November 29, 2005
Back Bay C (Sheraton)

10:30 AM NN5.1

Probing Interfacial Interactions of Biomaterials and Activation of Nanostructured Catalysts Using Atomic Force Microscopy. Jin Luo, Wei-Ben Chan, Nancy N. Kariuki and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

This presentation describes two areas of interfacial studies using atomic force microscopy (AFM). First, the ability to probe the adsorption of bacteria on surfaces is important for understanding the bacteria-surface interactions. We report findings on the use of AFM to probe the adsorption of *Pseudomonas aeruginosa* on atomically-smooth substrates of two different surface properties (hydrophilic and hydrophobic surfaces). Our aim is to demonstrate the viability of AFM in probing the bacteria-substrate interaction, which may have important implications to the understanding of biofilm formation. It is revealed that the interaction of the hydrophilic surface with the bacteria keeps the cell outer membrane relatively "rigid". In contrast, the interaction of the hydrophobic HOPG surface with the bacteria renders cell outer membrane relatively "soft". These two distinctive types of surface adhesion and interaction are discussed in terms of the structures and properties of lipopolysaccharide at the bacteria outer membrane. Second, the ability to control size and spatial properties of nanoparticle catalysts on the surface of a substrate or support material is critical in exploiting the unique catalytic activity of catalysts at the nanoscale. We report findings of an investigation of the thermal activation of molecular-wired gold nanoparticle assemblies on flat surfaces towards the development of the ability in size and spatial control. The morphological evolution at different temperatures was probed using AFM. The capping/wiring shell molecules can be removed to produce controllable particle size and interparticle spatial properties. The morphological properties are inherently linked to surface mobility, surface tension, and adhesion of nanoparticles on the substrate, which are supported by theoretical modeling of the thermally-induced sintering process. Implications of our findings to the controlled processing of catalyst nanostructures are also discussed.

10:45 AM NN5.2

Plasma Treatment of Carbon Nanotube AFM tips for Biological Imaging in Aqueous Environments. Chris R. So^{1,4}, You Li^{1,5}, Bishun Khare³, Joseph Leung², Andrew McMillian², Cattien V. Nguyen¹ and Meyya Meyyappan²; ¹Ames Center for Nanotechnology, ELORET/NASA Ames Research Center, Moffett Field, California; ²Ames Center for Nanotechnology, NASA Ames Research Center, Moffett Field, California; ³SETI, NASA Ames Research Center, Moffett Field, California; ⁴University of Washington, Seattle, Washington; ⁵Stanford University, Stanford, California.

Scanning force microscopy has a unique ability to image soft biological samples (including membrane structures of living cells) in aqueous environments. Recent developments have demonstrated the advantage of carbon nanotube (CNT) tips in scanning force microscopy for high lateral resolution and highly reproducible imaging. Moreover, because of the elastic buckling property of carbon nanotubes, it has been proposed that carbon nanotube tips can act as a compliant spring, hence limiting scanning force and minimizing damage to soft biological samples. We recently discovered that the configuration of the CNT tips could be irreversibly altered when submerged in an aqueous solution. This instability could be contributed to chemical incompatibility of the hydrophobic CNT sidewall and aqueous solution. We previously demonstrated that the physisorb of ethylene diamine to the CNT tip could circumvent this instability. This paper presents an alternative and permanent method of using oxygen plasma to partially oxidize the outer most sidewalls of CNT tips. The oxygen plasma treatment renders the sidewall of the nanotube tip hydrophilic, resulting in chemical compatibility with aqueous solutions for biological applications. Scanning electron microscopy data will be presented to correlate the morphology of CNT with the oxygen plasma oxidation process. The mechanical properties of plasma treated CNT tips based on atomic force microscope force measurement will also be presented. In addition, imaging data in aqueous solutions will be compared to those obtained in ambient environments for plasma treated CNT tips.

11:00 AM NN5.3

Chemomechanical mapping of living cell surfaces. Sunyoung Lee and Krystyn J. Van Vliet; Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Biomolecules bind to one another reversibly with pico- to nano-Newton scale forces that depend on rate of loading and affinity for one another. However, there exists no effective method with which these molecular level forces can be systematically detected on living cells. Here we report the distribution and binding activity of biomolecules on living endothelial cell surfaces, as imaged directly through measurement of these mechanical interactions between a molecule bound to a cantilevered scanning probe tip and a paired molecule bound to the specific receptor on living cell surface. Mapping of these interaction forces on living cell surfaces provides a powerful, quantitative approach toward imaging the real-time distribution and binding kinetics of key cell-surface receptors at the single cell level, and to identify new molecular indicators of cell state and processing of external mechanical cues.

11:15 AM NN5.4

Electromechanical Imaging of Biological Systems by Scanning Force Microscopy. Alexei Gruverman¹, Brian J. Rodriguez¹ and Sergei V. Kalinin²; ¹North Carolina State University, Raleigh, North Carolina; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Functional properties of biological systems are determined by an intricate set of mechanical and electromechanical interactions on the length scales that span several orders of magnitude: from macro to nano. The main motivation of studying electromechanical properties in biosystems is to understand the relationship between physiologically generated electric fields and mechanical properties on the molecular, cellular and tissue levels. Macroscopic studies of biological systems are inherently complicated by the hierarchical structure of these materials, thus necessitating studies of their properties from mesoscopic to molecular levels. Until recently, progress in this direction has been hampered by the lack of techniques capable of monitoring the electromechanical response of microscopic samples. In this paper, we demonstrate application of Piezoresponse Force Microscopy (PFM) to nanoscale characterization of electromechanical behavior in biological systems. Such different materials as human tooth, cartilage, collagen film and a butterfly wing, have been chosen for these experiments to demonstrate the general applicability of SPM to probing the bioelectromechanical behavior at the nanoscale. We demonstrate the simultaneous acquisition of the topographic and electromechanical maps of these biological systems along with local spectroscopy measurements. The piezoelectric activity found in butterfly wings is interpreted based on the relative orientation of chitin molecules and correlation of the piezoelectric behavior with the wing morphology and elasticity map has been discussed. The future prospects for application of electromechanical SPM for characterization of complex biological systems are discussed. Research is partially supported by ORNL SEED funding and DOE (Contract DOE-AC05-00OR22725).

11:30 AM NN5.5

DNA Nanoarrays for High Sensitivity Bioanalysis and Detections. Nabil A. Amro¹, Mike Nelson¹, Linette Demers² and Robert Elghanian³; ¹NanoInk, Inc, Chicago, Illinois; ²Sg2, LLC, Evanston, Illinois; ³International Institute for Nanotechnology, Evanston, Illinois.

Miniaturized nucleic acid, in the form of nanoscale spotted arrays, will dramatically enhance the sensitivity and spatial density of chip-based bio-assays. These nanoarrays will improve applications ranging from point-of-care diagnostics to genomic arrays used in basic research by enabling the development of next generation screening technologies that are faster, more sensitive, more reliable, and possibly more cost effective than those presently available in the life sciences market. Nanoscale nucleic acid bioarrays can be printed using Dip Pen Nanolithography (DPN), a new direct-write patterning technology which delivers sub-micron sized features of DNA or protein onto solid surfaces. This printing technique offers significant advantages over current microarray printing technologies that suffer from poor spot to spot reproducibility in terms of size, shape, and oligonucleotide density, as well as better reproducibility across microarray slides. Preliminary work has demonstrated that the DPN technique can be used to deposit 21mer synthetic oligonucleotides on surfaces with extremely uniform geometry and spot sizes ranging from sub-100 nm to several microns. DNA spots printed by the DPN method form stable nanostructures on the substrate and exhibit selectivity in binding to complementary oligonucleotides. Thus, DPN can be used to generate uniform features of synthetic DNA far smaller than those obtained with other spotting or photolithography techniques. We will describe current DPN nanoarray printing and readout technology and as well as our progress towards integrating the DPN process with MEMS and microfluidic pen systems for ultra-high throughput printing.

SESSION NN6: Scanning Probe Applications in Organic and Polymeric Materials
Chair: Nicholas Spencer
Tuesday Afternoon, November 29, 2005
Back Bay C (Sheraton)

1:30 PM NN6.1

Effect of the electrospinning process on the morphology and molecular chain orientation in electrospun PS/clay nanocomposites fibers. Yuan Ji, Bingquan Li, Shouren Ge, Jonathan Sokolov and Miriam Rafailovich; Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, New York.

Electrospinning is a rapid process during which the extremely large shear force induced by the electrical field on the fibers can lead to the molecular chain orientation along the fiber axis direction. In this

article, the surface nanomechanical property of electrospun PS/clay nanocomposites fibers as a function of fiber diameter and temperature was studied using a novel technique, Shear Modulation Force Microscopy (SMFM). A dramatic increase of the surface shear modulus below the glass transition temperature was observed, which results from the molecular chain orientation during electrospinning. IR-dichroism and laser birefringence measurements were conducted to confirm the molecular orientation in the electrospun fibers. The morphology and interior structure change of the electrospun fibers at different clay concentrations were also investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). A highly aligned montmorillonite layer structure was obtained at a clay concentration of 4wt% due to the high shear flow during electrospinning. Supported by NSF-MRSEC

1:45 PM NN6.2

Molecular orientation imaging with sub 10-nm resolution by Vector Piezoresponse Force Microscopy. Sergei V. Kalinin¹,

Brian J. Rodriguez^{1,2}, Jacqueline Hanson², Stephen Jesse¹, Arthur P. Baddorf¹, Vincent Meunier³ and Alexi Gruverman²; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ³Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Rapid development of nanoscience and nanobiology necessitates development of tools capable of structural characterization on the nanometer and atomic scale. Here we demonstrate that to obtain quantitative molecular orientation data, the measured signal should be (a) related to a rank three tensor property and (b) be independent of SPM probe geometry or easy to calibrate. These criteria limit the possible signals to piezoelectric response and optical second harmonic generation. We demonstrate an approach for molecular and crystallographic orientation imaging on sub-10 nanometer scale using Piezoresponse Force Microscopy. An in-depth analysis of the image formation mechanism is performed and it is shown that, unlike most SPMs, PFM is not sensitive to tip geometry. From the measured electromechanical response vector, local molecular or crystallographic orientation can be reconstructed using a simple theory. The PFM molecular imaging approach is demonstrated on two classes of materials including ferroelectric thin films and calcified tissues. Crystallographic orientation imaging is demonstrated on a model system of lead titanate ferroelectric thin film using three dimensional data vector data obtained for different sample orientations. In the biological systems, the properties are determined by the relative ordering and orientation of a relatively small number of biopolymers, such as collagen. Here, we employ the fact that most biopolymers that combine optical activity and polar bonds are strongly piezoelectric. The applicability of Vector PFM to biological systems is demonstrated on a variety of calcified tissues. The vector electromechanical response of a bundle of protein molecules in human tooth dentin has been visualized with 5 nanometer resolution. Imaging of the local orientation from Vector PFM data is illustrated. Due to a lack of macroscopic electromechanical data, the imaging is limited to semiquantitative and the limitations of this approach are discussed. The potential for calculation of piezoelectric properties of biomolecules, for which macroscopic properties are unavailable, using first principles theory, is discussed. The ubiquitous presence of piezoelectricity in biopolymers and many inorganic materials suggests that Vector PFM has exceptional potential for orientation imaging on the sub-10 nanometer length scale. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

2:00 PM *NN6.3

Subnanometer-resolution Imaging of Molecules in Liquid by Dynamic Force Microscopy. Hirofumi Yamada, Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan.

Dynamic force microscopy (DFM) using frequency modulation (FM) detection has been widely used for the atomic-scale investigations of various materials such as metals, semiconductors, insulators and organic molecules [1]. In FM detection tip-sample short-range interaction forces are sensitively measured by a frequency shift of a sharp cantilever resonance. All the high-resolution FM-DFM observations have been performed in UHV condition because of the high quality (Q-) factor of the cantilever resonance in vacuum, which usually exceeds 10,000. Imaging in liquid, however, is indispensable for the applications to nanobiology where visualization of individual biomolecules such as proteins and DNAs is essentially important. A major difficulty in DFM working in liquid originates from the fact that the Q-factor is extremely reduced due to the hydrodynamic interaction between the cantilever and the liquid. This reduction of the Q-factor directly connects to the decrease in the force sensitivity and consequently in the spatial resolution. In addition, the stable

cantilever oscillation in FM detection is often heavily perturbed. We have recently succeeded in subnanometer-scale imaging of organic molecules in liquid by FM-DFM [2, 3]. The difficulty was overcome mainly by the use of the small amplitude mode ($A < 1$ nm) and the noise reduction (17 fm/ $\sqrt{\text{sqrthz}}$) in the cantilever deflection sensor, leading us to the success in high-resolution DFM imaging in the low Q-factor environment. A cleaved surface of a polydiacetylene (2,4-hexadine-1,6-diol bis[*p*-toluene sulfonate]) single crystal was imaged in pure water. The herring bone structures of the side groups (*p*-toluene sulfonate) was clearly detected. Furthermore, purple membrane consisting of hexagonally packed bR (bacteriorhodopsin) protein trimers was imaged in buffer solution. The success in high-resolution FM-DFM imaging in liquid has opened the new way to direct visualization of "in vivo" molecular-scale biological process. [1] H. Yamada, in "Non-Contact Atomic Force Microscopy", S. Morita, R. Wiesendanger, Springer, pp.193-212 (2002). [2] T. Fukuma, K. Kobayashi, K. Matsushige and H. Yamada, Appl. Phys. Lett., 86, 193108-1 (2005). [3] T. Fukuma, M. Kimura, K. Kobayashi, K. Matsushige and H. Yamada, Rev. Sci. Instrum., 76, 053704 (2005).

3:30 PM NN6.4

Nano-thermal Analysis (Nano-TA) at sub-100 nm Spatial Resolution. Azzedine Hammiche^{2,4}, Michael Reading^{1,4}, T. L. Wright³, J. Lee³, W. P. King^{3,4}, H. Pollock⁴ and R. Shetty⁴; ¹Chemical Sciences & Pharmacy, University of East Anglia, Norwich, United Kingdom; ²Lancaster University, Lancaster, United Kingdom; ³Georgia Tech, Atlanta, Georgia; ⁴Anasys Instruments, Westlake Village, California.

In micro-thermal analysis [1-3], materials are identified by the detection of phase changes when a SThM probe is used to apply a temperature ramp to the sample. However, to date the published literature includes no descriptions of micro-TA having been performed at a spatial resolution of better than a few microns. This paper reports sub-100nm resolution with a new generation of thermal probes [4] that have been specially tailored for this application. These probes also provide for imaging in tapping mode with typical AFM resolution at sub-50nm. Furthermore images in which the contrast between the phases depends on differences in viscoelastic properties can be acquired at different tip temperatures. By acquiring images at above and below transition temperatures structure can be more easily seen and phases identified. This approach has significant advantages over the more established technique of heating globally with a temperature-controlled sample stage [5] for several reasons including: 1. Global heating of the sample will often induce structural changes and so the structure imaged might not be the as-received structure. With local heating the duration at elevated temperatures can be as short as 1 ms and the sample temperature rise is highly localized. Since only the tested part of the sample is heated and even then for an extremely short time, there is reduced opportunity for structural changes to occur. Even where damage occurs, there will be plenty of undamaged surface available for further study. 2. Where the low transition material is the matrix, heating above this temperature will destroy the sample making it impossible to study phases with higher temperature transitions. 3. With local heating it is possible to examine samples of any size without sample preparation, whereas on a hot stage there can be considerable temperature gradients across the thickness of a sample, even to the extent that the bottom of the sample can disintegrate before the top achieves the desired temperature. We have also demonstrated how thermal probes can be used to pick up small quantities of material from selected locations [6] and then deposit them onto a different surface in preparation for chemical analysis. Hot-tip force distance curves can reveal unexpected information about surfaces even on industrial samples. Data will be presented on a variety of polymer and pharmaceutical samples illustrating how nanometre scale structures can be seen and analysed and how the thermorheology of surfaces can give unique insights into surface properties. References: 1. Hammiche., Review of Scientific Instrumentation, 6712, 1996, 4268-4273. 2. Reading M.: , Macromol. Symp., 167, 2001, 45-62 3. Pollock H.M.: J. Phys. D: Appl. Phys. 34 (2001) R23-R53 4. W. P. King; Journal of Microelectromechanical Systems, vol. 11, pp. 765-774, 2002. 5. Grandy, D. B.; Macromolecules 33, 2000, 9348-9359 6. Reading M.: Vibrational Spectroscopy, 29, 2002, 257-260

3:45 PM NN6.5

In Situ Temperature-Dependent AFM Study of Structures in Poly (Ester Urethane) Materials. Marilyn Emily Hawley, Debra A. Wrobleksi, E. Bruce Orler and Rex P. Hjelm; Los Alamos National Laboratory, Los Alamos, New Mexico.

Characterization of the complex and evolving phase structure in Estane-like Poly (ester urethane) materials presents a particularly difficult challenge. The components in this system, methylphenylisocyanate with butanediol chain extender and poly (butylene adipate), segregate in crystalline hard segments (HS) and a rubber-like matrix of soft segments (SS). Further difficulties in

unraveling the origin of observed structures are due to incomplete phase segregation of the components. In previous studies on compression molded samples, AFM identified at least three different structures in materials ranging from 100% to 19% HS content: 10 nm thick long strands, phase segregation of a 10 nm harder phase in a soft matrix, and 40 to 100 nm thick strands or rods. These structures depending on composition and fabrication method, and evolve over time. In an attempt to understand the origin of these structures, AFM in situ heating characterization experiments were performed on samples with a range of HS to SS composition and the structural information was compared to that of the pure components. The disappearance of the 10 nm strands near the melting temperature of the pure SS suggests that they are SS rich. The larger strands persist up to at least 180 C, which is consistent with the HS melting temperature.

4:00 PM NN6.6

Oxidation Conditions for Octadecyl Trichlorosilane Monolayers on Silicon: A Detailed AFM-Study of the Effects of Pulse-Height and Duration on the Oxidation of the Monolayer and the Underlying Si-Substrate. Daan Wouters^{1,2}, Ron Willems^{3,4}, Stephanie Hoepfener^{1,2}, Cees F. J. Flipse^{3,4} and Ulrich S. Schubert^{1,2}; ¹Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; ²Dutch Polymer Institute (DPI), Eindhoven, Netherlands; ³Center for Nanomaterials, Eindhoven University of Technology, Eindhoven, Netherlands; ⁴Molecular Materials and Nanosystems, Eindhoven University of Technology, Eindhoven, Netherlands.

Using local probe oxidation of conducting and semi-conducting substrates, several groups have demonstrated sub 20 nm patterning of surfaces as well as the application of these patterns in both positive and negative subsequent etching procedures of, for example, silicon substrates. Self assembled monolayers (SAMs) of simple molecules have been employed as resist layers further improving the resolution or even claimed to increase the oxidation speed of the underlying SiOx/Si over bare substrates. Within the field the oxidative scanning probe lithography of organic self-assembled monolayers (e.g. octadecyl trichlorosilane (OTS) on silicon) has recently gained a lot of interest because it offers a very versatile platform for the build-up of complex systems. Although the important conditions for the local probe oxidation of silicon to silicon dioxide (humidity, bias voltage and pulse duration) have been studied extensively, the role of the self assembled monolayer remains underexposed. In this contribution we discuss the influence of the applied bias voltage and the pulse duration on the local oxidation of OTS monolayers on SiOx/Si. This we do in terms of the formation of carboxylic acids end groups and/or the oxidation of the underlying silicon as observed by lateral force microscopy. This information is correlated to observed line heights obtained by contact-mode imaging in different directions as well as electrostatic force imaging. When performing local probe oxidation experiments on OTS monolayers, in principle two reactions can take place: firstly the conversion of the top methyl groups of the OTS molecules in the monolayer into carboxylic acids end groups, secondly the local probe oxidation of the silicon substrate, resulting in the local growth of silicon dioxide. The formation of silicon dioxide leads to an actual increase in height, whereas the formation of acid groups leads to a change in height that depends on the scanning direction as a result of cross-talk between the friction and the height signals. This was confirmed by using x-modulated friction force imaging. The fact that the observed height changes sign when the scan direction is reversed, was used as an indication for the formation of carboxylic acid end groups. These observations were used to determine the parameter space in which either reaction takes place. We found that for a fixed bias voltage, the formation of silicon dioxide takes longer than the conversion of OTS to carboxylic acid end groups. In general, the oxidation of OTS takes one to two orders of magnitude less time than the growth of silicon oxide. We also confirmed the presence of negative charges on the surface with electrostatic force microscopy. These charges, however, are not influencing the mechanism of reactivity of subsequent surface functionalization steps, as these charges disappear in time whereas the surface-reactivity does not.

4:15 PM NN6.7

Applications of Chemical Force Microscopy in DUV and EUV Lithography. John T. Woodward¹, Lori S. Goldner¹, Jeeseong Hwang¹, Bryan D. Vogt², Vivek M. Prabhu², Eric K. Lin², Kwang-Woo Choi^{3,2}, Robert P. Meagley³ and Michael J. Leeson³; ¹Optical Technology Division, NIST, Gaithersburg, Maryland; ²Polymers Division, NIST, Gaithersburg, Maryland; ³Intel Corporation, Santa Clara, California.

Current (DUV) and future (EUV) lithography nodes are based upon chemical amplification, where a photoacid is exploited as a catalyst to selectively alter the resist solubility through chemical modification. In this process, radiation exposure generates a photoacid that catalyzes

a thermally activated deprotection reaction during post-exposure bake. These lithographic steps generate a latent chemical image of the printed features that is developed with a selective solvent, typically aqueous base. It is not until after this final step that the quality of the lithographic pattern can be assessed with typical metrologies such as SEM. Here, we illustrate that chemical force microscopy (CFM) is capable of distinguishing between the chemistries relevant to the photolithographic process and thus has the potential to measure the distribution of chemical species after each stage of the lithographic process. Information about the quality of these intermediate stages will greatly aid the optimization of the overall process. We will discuss our methodology for developing CFM into a metrology tool capable of the chemical sensitivity and spatial resolution required to assess current and future lithographic processes.

4:30 PM NN6.8

Using In situ atomic force microscopy and single molecule confocal microscopy to investigate the control of organic molecules on the growth of inorganic materials.

James J. DeYoreo¹, Patricia Dove², Chad E. Talley¹, Bart Kahr³ and Ryan E. Sours³, ¹Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California; ²Department of Geosciences, Virginia Tech, Blacksburg, Virginia; ³Department of Chemistry, University of Washington, Seattle, Washington.

Throughout a wide range of environments, living organisms interact with, modify, and exploit inorganic surfaces. Whether through production of mineralized tissues, extra-cellular deposition of mineralized waste, or the scavenging of electrons from mineral substrates, proteins, peptides, and other bio-organic molecules mediate these processes. Prior to the advent of atomic force microscopy, our understanding of how organic molecules interacted with crystalline substrates was limited to macroscopic and spectroscopic studies in which the connection between molecular scale structural models and macroscopic effects was primarily conjectural. AFM is inherently capable of both operating in fluids and imaging the terrace-ledge structure of crystal surfaces. Consequently, over the past decade, it has had a dramatic impact on our understanding of the mechanisms by which bio-organic molecules modify crystal growth and dissolution. Moreover, it has led to estimates for the thermodynamic and kinetic parameters that characterize those mechanisms. More recently, the merging of force microscopy with confocal microscopy has enabled the simultaneous imaging of surface morphology and tracking of impurity dynamics at the level of atomic steps and single molecules respectively. In this talk, we review some of the highlights from the past decade that show how in situ scanned probe imaging has changed our understanding of organic and macromolecular modification of crystallization. SPM studies have altered our thinking about how the mechanism of stereochemical recognition controls crystal shapes, replacing the matching of molecular modulators to new crystal faces with step-specific binding on existing faces. They have revealed serious discrepancies between previously well-accepted theories of crystal growth modification and led to new models for mineral growth that displaces the paramount role of thermodynamic controls in favor of kinetic controls. SPM studies have revealed new families of step structures, unexpected switching of growth shapes and rates with peptide chain lengths and chemistries, and even the emergence of chirality in crystal morphologies. Finally, we point out some of the technical challenges associated with quantitative measurement of dynamic processes, and point out new directions for SPM investigations in the field of biological crystallization, primarily associated with the controls of biological templates on mineral nucleation. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

4:45 PM NN6.9

Effects of Solvents, Surfactants and SARA Fractions on Wettability. **Kamlesh Kumar**, Kishore K. Mohanty and Eric K. Dao; Chemical Engg, University of Houston, Houston, Texas.

Wettability, the tendency of a surface to be preferentially wet by one fluid phase, is very important to multiphase transport properties and adsorption in microporous media. The polar components of crude oil can adsorb on the rock/mineral surface and hence alter their wetting properties. One of the goals of this work is to study the role different SARA fractions (saturates, aromatics, resins and asphaltenes) play in the wettability of a mineral surface. Another objective of this work is to study the effect of solvents, namely toluene, decalin and cyclohexane on the wettability of oil-aged mineral surfaces. Using AFM (Atomic Force Microscopy), the topography of the oil-aged surfaces is studied and the degree of hydrophobicity is quantified by surface force measurements using specially coated cantilever tips. The topography images show that toluene is a better solvent than decalin and cyclohexane. It was also observed that the force of adhesion for minerals aged with just the asphaltene fraction is similar to that of

the whole oil. Surfactant injection is a well known enhanced oil recovery technique. However, the exact mechanism of wettability alteration using surfactants is still unknown. In this study, we also focus on mechanism of wettability alteration by surfactants using AFM. A few surfactants have been identified to alter the wettability of the mineral surfaces. The adhesion forces between modified AFM tips and the surfaces are measured before and after surfactant treatment to characterize the wettability of the surface.

SESSION NN7/Y5: Joint Session: Surface Engineering -
Scanning Probe Microscopy Session

Chair: Scott Sills
Wednesday Morning, November 30, 2005
Back Bay C (Sheraton)

8:00 AM *NN7.1/Y5.1

Scanned Probe Microscopy-based Nanomechanics and Microtribology of Solid Lubricants. **Kathryn J. Wahl**, Richard R. Chromik and Gunyoung T. Lee; Tribology Section, U.S. Naval Research Laboratory, Washington, District of Columbia.

Friction, wear and endurance of solid lubricant films are controlled by interfacial processes involving "third body" transfer films. These third body films are thin (nanometers to microns), inhomogeneous on the micron scale, and differ from the originating solid lubricant film both chemically and mechanically. *In situ* tribological studies have shown that these films also exhibit dynamic rheological properties that depend strongly on sliding conditions. In this talk, we will illustrate how spatially resolved, surface sensitive nanomechanics and microtribology experiments can be used to study solid lubrication processes. SPM-based instrumented nanoindentation is used to correlate nanomechanical properties of the interfacial films with macroscopic tribological response. Also, by rastering the indenter tip laterally, instrumented indentation apparatus can be used to examine microscale sliding processes and address scaling effects in solid lubrication. In both cases, knowledge of indenter/counterface geometry, penetration depth, load, and position are key, enabling evaluation of the lubrication mechanisms as well as comparison with contact mechanics models. Ultimately, these micro- and nanoscale approaches can provide new insight into tribological phenomena at all scales.

8:30 AM NN7.2/Y5.2

Measurements of Creep on an OTS Monolayer Coated Microactuator. **Alex D. Corwin¹**, Robert W. Carpick², Erin E. Flater², Robert W. Ashurst³ and Maarten P. de Boer¹; ¹MEMS Technology, Sandia National Labs, Albuquerque, New Mexico; ²Engineering Physics, University of Wisconsin - Madison, Madison, Wisconsin; ³Chemical Engineering, Auburn University, Auburn, Alabama.

Organic monolayer coatings are used in contacting micromachined devices to reduce friction, wear, and adhesion. We have developed a "nanotractor" actuator, which is a friction-based microelectromechanical (MEMS) device that can be used to make sensitive measurements of both adhesion and static and dynamic coefficients of friction. We have used the nanotractor to look at a variety of self-assembled monolayer (SAM) coatings, including octadecyltrichlorosilane (OTS), (tridecafluoro-1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane (FOTAS), as well as uncoated devices dried in a critical point drier (CPD) using carbon dioxide as the supercritical fluid. These are precisely the treatments used in actual MEMS devices, and the coatings are extremely effective in reducing adhesion. Measurements of friction show that at the micro-scale, friction is proportional to the sum of the adhesive and applied loads. Both coatings reduce static and dynamic friction compared with the uncoated devices, with the OTS coating being significantly more effective. However, our recent measurements with OTS show complex effects beyond simple reductions in the friction coefficient. In particular, OTS-coated devices show significant time-dependent creep even under an applied normal load large enough to prevent slip based on the measured coefficient of static friction. While FOTAS and CPD-treated films do not exhibit perceptible creep within our measurement resolution of 10 nm, we have measured motions up to three microns occurring over a period of four minutes for the OTS coating. We hypothesize that OTS, consisting of an 18 carbon chain and significantly longer than FOTAS molecules, enables the entanglement and slow disentanglement of the chains, leading to the observed creep. We will discuss these results in comparison with single-asperity measurements of the same materials conducted with atomic force microscopy. We further examine the temperature dependence of the creep in the MEMS device using a thermal stage with 0.1 C temperature stability. Acknowledgment: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security

8:45 AM NN7.3/Y5.3

A few asperities determine the work of adhesion in nanometer contacts. Erik Thoreson¹, J. Martin² and N. A. Burnham¹; ¹Department of Physics, WPI, Worcester, Massachusetts; ²Analog Devices, Inc., Cambridge, Massachusetts.

The surface roughness of a few asperities and their influence on the work of adhesion is of scientific interest. Engineering and nanoscopic scale adhesion data have seemingly given contradictory results. Despite the importance of bridging the gap between the two regimes, little experimental work has been done, presumably due to the difficulty of the experiment, to determine how small amounts of surface roughness might influence adhesion data in between the two scales. To investigate the role of few-asperity contacts in adhesion, the work of adhesion was measured between different sized AFM tips (with different roughnesses) and sample surfaces that had well-controlled material properties. There were seventeen tips of four different types, with radii from 200 nm to 60 μm . The samples were unpatterned amorphous silicon dioxide die with two types of surface conditions (untreated and treated with a few angstroms of vapor deposited diphenylsiloxane). We observed that the work of adhesion decreased as the radius of the AFM tip increased, which was contrary to all continuum-mechanics model predictions. To explain this behavior, we assumed that the interactions between the AFM tip and sample were additive, material properties were constant, and that the AFM tip, asperities, and sample surfaces were of uniform density. Based on these assumptions, we calculated a simple correction due to the surface roughness of the AFM tips. The simple correction for the surface roughness resulted in the expected independence of the work of adhesion from radius, but the magnitudes were higher than expected. Normal and heat-treated AFM tips have minimal surface roughness and result in magnitudes that are more reliable. The relative uncertainty for the work of adhesion was 15%. In this presentation, we derive how the cantilever and tip parameters contribute to the measured work of adhesion and show how the corrected results compare with theory. Although much work is still needed, the work presented here should progress the understanding of adhesion between the engineering and nanoscopic scale.

9:00 AM NN7.4/Y5.4

Mechanical load assisted dissolution: Influence of contact loads and residual stresses. Andrew Mitchell and Pranav Shrotriya; Mechanical Engineering, Iowa State University, Ames, Iowa.

Mechanical load assisted dissolution is identified as one of the key mechanism governing material removal in phenomena such as fretting corrosion or chemical mechanical planarization (CMP). Repeated contact of biomedical implants in a corrosive physiological environment leads to fretting corrosion resulting in formation of soluble and particulate debris that may induce a cascade of inflammatory events or failure of the implant. Similarly, CMP involves removal of material through small particles abrading the surface in a reactive environment. While it is well known that stress affects the dissolution rate of material the exact mechanisms governing stress-assisted dissolution are still not well understood. In order to identify the governing mechanism, dissolution of a stressed metallic surface subjected to single asperity contact is investigated. For this study, specimens are mounted in four point bending configurations such that a range of stress levels are applied to the specimen surface. The testing configurations are designed for easy accessibility to facilitate in-situ mechanical stimulation and imaging by Atomic Force Microscope (AFM). To develop a thorough understanding of stress effects on dissolution two material systems were investigated; CoCrMo (ASTM F75) commonly used in total hip and knee replacements, and a Cu alloy commonly used in the investigation of CMP process. Using the tip of an atomic force microscope (AFM) as a well characterized //asperity, controlled contact forces are applied to mechanically stimulate the loaded specimen surface in ambient and oxidizing environments. This would be analogous to a wear particle (the AFM probe) coming into contact with the stressed surface of an implant or work piece. Volume of the material removed is measured to determine the dissolution rate as a function of applied surface stress and contact loads. In addition, a kinetic model of stress-assisted material dissolution is developed to analyze the experimental observations and identify critical stress and loading levels required to initiate accelerated material dissolution.

9:15 AM NN7.5/Y5.5

In - Situ Raman Tribometry Studies on Adaptive Nanocomposite Coatings. Richard Chromik^{1,2}, Colin Baker^{2,3}, Andrey Voevodin³ and Kathryn Wahl¹; ¹Code 6176, Naval Research Laboratory, Washington, District of Columbia; ²Department of Physics, North Carolina State University, Raleigh, North Carolina; ³Materials and Manufacturing Directorate, Air Force Research

For tribological applications where temperature and humidity vary over a wide range, the design of a suitable coating system becomes especially challenging. Solid lubricant materials typically perform best within a narrow range of environmental conditions. One solution is to develop nanocomposite coatings with multiple phases, each with advantageous tribological properties for a given environment. Previous research on nanocomposite coatings containing yttria stabilized zirconia (YSZ), diamond like carbon (DLC), Au and MoS₂ has demonstrated frictional adaptation to that of the component exhibiting the lowest friction coefficient for humid, dry or elevated temperature conditions. *Ex situ* characterization tied this behavior to changes in the chemistry of the transfer film. Using a custom-built reciprocating tribometer, we have studied the transfer film formation, chemistry and dynamics of YSZ/DLC/Au/MoS₂ coatings as a function of humidity and sliding cycles. Steady state friction coefficients were 0.07-0.08 in ambient conditions (45-55%RH) and 0.04-0.05 in a dry nitrogen environment (4-6%RH). A transparent sapphire counterbody allowed for *in situ* video imaging of the sliding contact and chemical analysis of the transfer film using micro-Raman spectroscopy. Both of these analysis techniques, as well as *ex situ* Raman and optical profilometry, indicated that the transfer film is thicker for dry environments than for wet. Additionally, the velocity accommodation modes in dry and humid environments were different – dry conditions resulted in primarily interfacial sliding while wet conditions allowed for some transfer film shearing. However, for both environments, debris exchange between the counterface and the track was very dynamic and, in the case of dry conditions, led to frictional spiking. During humidity changes, images of the contact revealed that the transfer film breaks down and re-grows, but at a slower rate than the friction adaptation.

9:30 AM NN7.6/Y5.6

Characterization of Tribo-chemistry in Hard Nanostructured Carbon Materials using PEEM-NEXAFS Spectromicroscopy. Anirudha V. Sumant¹, David Grierson¹, Jason Bares¹, Mike Abrecht², Brad Frazer², Gelsomina De Stasio², Orlando Auciello³, John Carlisle³, Thomas Scharf⁴, Mike Dugger⁴, Thomas Friedmann⁴, John Sullivan⁴ and Robert Carpick¹; ¹Engineering Physics, University of Wisconsin at Madison, Madison, Wisconsin; ²Department of Physics, University of Wisconsin at Madison, Stoughton, Wisconsin; ³Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ⁴Sandia National Laboratories, Albuquerque, New Mexico.

Tribo-chemistry of sliding surfaces in contact plays an important role in determining the wear and friction properties of interfaces from macro to nano-scale applications. Ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C) films are particularly promising materials for a range of demanding applications to macro, micro, and nanodevices, because of their exceptional mechanical and tribological properties. However, the mechanisms controlling friction and wear of UNCD and ta-C are not well understood because of lack of understanding of tribo-chemical processes at play. Furthermore, as-deposited ta-C films have high residual stresses, and full stress relief is possible by post-annealing at elevated temperatures (650 oC). However, no systematic experimental studies were previously reported to understand the surface chemistry and bonding configuration of these films after annealing, which most likely will affect their tribological properties. We present studies aimed at elucidating the fundamental tribo-chemical mechanisms of wear and friction in UNCD and ta-C films. We have performed fretting and sliding wear measurements using a ball-on-disc apparatus for UNCD and ta-C films in contact with both self-mated and Si₃N₄ balls in ambient and controlled atmosphere conditions. The micron-scale wear tracks produced on these films have been analyzed by atomic force microscopy (AFM) and PEEM-NEXAFS (PhotoElectron Emission Microscopy combined with Near-Edge X-ray Absorption Fine Structure) spectromicroscopy to obtain quantitative information on structural modifications and chemical changes inside the wear track. The ability of the PEEM-NEXAFS technique to spatially resolve (10 nm in ideal case) and chemically characterize regions of interest is unparalleled and therefore ideally suited for this work. The results show for the first time that it is possible to detect chemical changes with great details occurring within the micro-scale wear track of these materials. Furthermore, we are able to establish correlations between spectroscopically-identified chemical changes within the wear track and corresponding changes in the friction coefficient recorded during tests. In the case of a UNCD film in contact with a Si₃N₄ ball, we see formation of SiOx complexes within the wear track, and corresponding increases in friction coefficient. In the case of a ta-C film in contact with Si₃N₄ ball, we observed a decrease in friction coefficient after annealing, and complex changes in the carbon bonding configuration on the surface. We will discuss the chemical changes within the wear tracks, the possible mechanisms behind them, and the resulting effect on friction and wear behavior in these films.

9:45 AM NN7.7/Y5.7

The Effect of Surface Atomic Structure on the Nanotribology of Ultrananocrystalline Diamond and Tetrahedral Amorphous Carbon Thin Films. D. S. Grierson¹, A. V. Sumant¹, J. E. Gerbi², J. Birrell³, O. Auciello^{5,4}, J. A. Carlisle^{5,4}, T. A. Friedmann⁶, J. P. Sullivan⁶ and R. W. Carpick¹; ¹Engineering Physics, UW-Madison, Madison, Wisconsin; ²University of Illinois at Urbana-Champaign, Champaign, Illinois; ³Advanced Diamond Technologies, Inc., Champaign, Illinois; ⁴Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ⁵Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; ⁶Sandia National Laboratory, Albuquerque, New Mexico.

High performance carbon-based thin films are attracting interest as candidate materials to enhance the tribological characteristics of mechanical components from the macro- to the nanoscale. These materials have been studied at the macroscale, and the resulting tribo-mechanical properties have been shown to be excellent. However, at the micro- and nanoscale, little is known about the tribological properties and how they are affected by the surface atomic structure. We have gained new fundamental insights into how differences in bonding structure, film microstructure, surface chemistry, and chemical environment produce different nanotribological behavior. We have investigated two distinct carbon-based thin film materials: ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C). To understand the surface chemistry of these materials, we use near edge x-ray absorption fine structure (NEXAFS) spectroscopy to determine the chemical composition and the nature of the bonds in the near-surface region. To study the corresponding nanotribological properties, we use the atomic force microscope (AFM) to measure the work of adhesion and frictional forces between diamond AFM tips and the materials of interest. We find that the nanotribological properties depend sensitively on the surface chemistry and bonding. In the case of UNCD, we can lower the work of adhesion between a diamond tip and the UNCD surface by terminating the surface with hydrogen. We find that the adhesion can reach the van der Waals' limit ($<30 \text{ mJ/m}^2$) by this process, and we find that adhesion and friction are significantly lower than for silicon self-mated interfaces. Studies of ta-C demonstrate how bonding structure and nanotribological properties are affected by thermal annealing, which is a critical step in the film synthesis required for relieving internal stresses. Specifically, we find that annealing ta-C above 600° C increases the amount of sp^2 -bonded carbon near the surface (graphitization), but the work of adhesion between the diamond tip and the ta-C is not affected. Preliminary results indicate that friction forces are modestly reduced by this process. We will discuss possible mechanisms that account for this surprising behavior. We will also discuss how our results can be used to tailor the surfaces of carbon-based materials to optimize their tribological response. Part of this work was funded by Sandia. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Part of this work was also supported by the US Department of Energy, BES-Materials Sciences, under Contracts DE-FG02-02ER46016 and W-13-109-ENG-38 and the Air Force Office of Scientific Research under Contract FA9550-05-1-0204.

SESSION NN8: Scanning Probe Applications in Tribology
Chair: Ernst Meyer
Wednesday Morning, November 30, 2005
Back Bay C (Sheraton)

10:30 AM NN8.1

Transitions in Atomic-Scale Stick-Slip Friction Behavior on Graphite due to System Stiffness. In-Ha Sung, Rachel J. Cannara and Robert W. Carpick; Engineering Physics, Univ. of Wisconsin-Madison, Madison, Wisconsin.

To obtain a fundamental understanding of the origin of atomic-scale stick-slip friction, an experimental investigation of the frictional behavior between nano- and micro-scale tips and a highly oriented pyrolytic graphite (HOPG) surface were performed using atomic force microscope (AFM) cantilevers with different stiffnesses and tips. Strong interest in this research arises from the myriad applications for carbon-based materials at sliding interfaces, including as wear-resistant coatings and in biosensors, hard disk drives and micro/nano-electromechanical systems. The primary objective of this research is to determine how atomic-scale stick-slip depends on the mechanical and material properties of the system. For the purpose of this work, three different cantilevers, which have bare (uncoated) tips, coated tips and colloidal particles attached in place of the tip, respectively, were used in the experiments. Each of these cantilevers has different dimensions and thus, different normal and lateral

stiffnesses. The tips are coated with distinct materials, namely silicon, silicon nitride, amorphous carbon, and graphite flakes, and they come in a range of shapes and sizes (from 20 nm to $10 \mu\text{m}$ diameter). Experimental results show that stick-slip friction behavior occurs even when the colloidal probes with a particle of a $10 \mu\text{m}$ in diameter, which have a relatively large contact area and lack a well-shaped apex, were used. This indicates that atomic stick-slip friction may be a more common phenomenon than it is currently thought to be. Also, unlike the well-known normal stick-slip behavior that shows a single stick-slip event per unit cell, we observed that multiple stick-slip events occur in the case of relatively low lateral cantilever stiffness, regardless of the contact stiffness of system. Based on the experimental results, the relationship between the range of stick-slip behaviors observed, contact stiffness, tip material, and cantilever type was carefully investigated. The results qualitatively correlate with a theoretical prediction for the onset of multiple slips for low cantilever stiffnesses [1]. [1] K. L. Johnson, J. Woodhouse, Tribol. Lett. 5, 155 (1998)

10:45 AM NN8.2

Probing the Morphology and Tribology of Complex Fluid Films. Greg Haugstad¹ and Andrew Avery²; ¹University of Minnesota, Minneapolis, Minnesota; ²Unilever Research, Port Sunlight, United Kingdom.

In the first decade following the invention of atomic force microscopy (AFM) in 1986, several operating modes were developed to differentiate materials via tip-sample interactions. Modes such as friction force under sliding contact or phase lag under AC interaction were found to contrast near-surface polarity, charge, potential, (visco)elasticity and crystallinity. Although these modes have been powerful contrasting agents even for novice users, detailed mechanistic understandings have been few. During the same time there were biophysical and biochemical AFM studies to measure ligand-receptor interactions, gauge persistence length, and sense folding/unfolding and other conformational transformations in chain molecules. These latter methods utilize force spectroscopy, where tip-sample distance is cycled to provide a force-derived fingerprint of molecular behavior, albeit at single locations. Today, with high capacity data transfer, storage and manipulation, it is feasible to combine high resolution imaging and detailed distance-dependent measurements. A methodology is presented for interrogating emulsion-delivered, polymer liquid/surfactant films heterogeneous in thickness (one to tens of nanometers), important to personal care applications. Multiple AFM modes including both lateral position and distance dependent measurements are utilized to elucidate 2D regions of liquidy character interspersed in regions of solid character. Images are radically different in a mode of quasistatic contact compared to dynamic contact, and further in regimes of net repulsive compared to net attractive dynamic contact. Approach-retract cycles are explored in each regime to develop essential understandings of probe-film interaction, and thereby correct interpretations of images (height, phase, friction). The implementation exploits the power of spatially mapped approach-retract measurements in conjunction with special data reduction algorithms; some results were obtained with the relatively new digital pulsed force mode (D-PFM). The extremely high data acquisition and analysis capabilities of D-PFM enabled a level of understanding of PDMS-CTAC complex films unachievable with standard modes of operation. In addition, capillary transport of selected film components up the AFM tip was discovered and utilized diagnostically to further reveal intriguing aspects of film morphology and dynamics.

11:00 AM *NN8.3

Probing molecular dynamics and the influence of finite size effects in polymeric systems. Scott Sills¹ and Rene M. Overney²; ¹IBM Almaden Research Ctr., San Jose, California; ²Chemical Engineering, University of Washington, Seattle, Washington.

Nanotechnologies involving polymers and organic thin films are faced with a competition between material and device length scales. In these systems, the quest for superior material and transport properties is faced with the underlying degrees of freedom available to particular molecular motions. This work highlights real-space probing techniques that are used to access molecular mobilities in nanoscopic systems. Using friction force microscopy (FFM), both the energetics involved in frictional dissipation and the length scale over which the energy is dissipated are linked to the intrinsic molecular relaxation processes in polystyrene. The introduction of dimensional constraints, either external (interfaces) or internal (crosslinks), leads to restricted freedoms and modified relaxation dynamics, which are explored with interfacial glass transition profiles obtained from shear-modulated force microscopy (SM-FM). The resulting generation of rheological gradients in confined regions is confirmed with nano-impact studies in thin films, and the interplay between material and device length scales is illustrated for high density recording in scanned-probe storage

devices.

11:30 AM NN8.4

The Effect of Physisorbed Glycoproteins on Friction between Model Surfaces Measured with Lateral Force Microscopy.
Nehal Ibrahim Abu-Lail¹, Gregory Jay³, Farshid Guilak² and Stefan Zauscher¹; ¹Mechanical Engineering, Duke University, Durham, North Carolina; ²Department of Orthopedic Surgery, Duke University, Durham, North Carolina; ³Department of Emergency Medicine, Rhode Island Hospital, Providence, Rhode Island.

Glycoproteins, such as lubricin and hyaluronic acid (HA), likely play a prominent role in the boundary lubrication mechanism in diarthroidal joints, where the superficial surface layer (SSL) of articular cartilage serves as the bearing surface. The loss or damage of the SSL likely initiates cartilage damage and often leads to joint diseases such as osteoarthritis. Although the tribological properties of the SSL are widely studied, the details of the boundary lubrication mechanism are poorly understood. This is mainly due to the chemical and morphological heterogeneity of the cartilage surface. Here we present for the first time results of friction measurements between w-substituted alkane thiol modified model surfaces in presence of physisorbed lubricin. Friction was measured by lateral force microscopy using chemically functionalized colloidal probes. We investigated a range of lubricin concentrations, chosen to bracket the concentration of 200 mg/ml found in the synovial fluid of rabbits. Our results show that the coefficient of friction is low (0.045) for small lubricin concentrations (<200 mg/ml) and high (0.13) for large concentrations (>200 mg/ml). To estimate the adsorption of lubricin onto OH-thiol terminated surfaces we used surface plasmon resonance (SPR) experiments. These experiments showed that a monolayer formed at a lubricin solution concentration of 200 mg/ml. We also report on our experiments in which HA and lubricin act synergistically to reduce friction.

11:45 AM NN8.5

Friction force microscopy as a tool to probe local phase transitions. Robert Szoszkiewicz and Elisa Riedo; Physics, Georgia Institute of Technology, Atlanta, Georgia.

We study local nanoscopic friction forces between an atomic force microscope tip and a glass sample in a humid environment [1, 2]. We show [1] how and why it is possible to tune friction forces in a predictable way by changing either the sample temperature, or the humidity in the experimental chamber. We relate the friction behavior to confined water phase transitions. We find that the water gas-liquid phase diagram is the same at the macroscopic scale as well as at the nanoscopic tip-sample contact. Detailed friction measurements at varying sample temperature and humidity allow us also to extract information about kinetics of capillary condensation at the nanoscale [2]. At 40 % relative humidity we find that meniscus nucleation times increase from 0.6 ms up to 3.5 ms when temperature decreases from 332 K to 299 K. The nucleation times grow exponentially with inverse temperature $1/T$ obeying an Arrhenius law. We obtain a nucleation energy barrier of 7.8×10^{-20} J and an attempt frequency ranging between 10-100 GHz, in excellent agreement with theoretical predictions. These results provide direct experimental evidence that capillary condensation is a thermally activated phenomenon. References: [1] R. Szoszkiewicz, E. Riedo, submitted to Appl. Phys. Lett. (2005). [2] R. Szoszkiewicz, E. Riedo, submitted to Phys. Rev. Lett. (2005).

SESSION NN9: Mechanical Properties Studies with Scanning Probes

Chairs: Robert Carpick and Sheldon Wiederhorn
Wednesday Afternoon, November 30, 2005
Back Bay C (Sheraton)

1:30 PM *NN9.1

Fracture Properties of Oxide Glasses at Nanometer Scale.
Christian Marlière, ¹L.C.V.N., UMR 5587, University Montpellier 2 - CNRS, Montpellier, France; ²Tectonophysique, UMR 5568, University Montpellier 2 - CNRS, Montpellier, France.

Crack propagation phenomena are still one of the major challenges in engineering and fracture mechanics science. It is now well established that macroscopic mechanical properties such as resistance to rupture [1], friction between surfaces [2], cohesion of cement-like materials, etc. are directly connected to atomic-scale details. One important example is the very commonly used class of materials, oxide glasses, and its most limiting property: its poor resistance to fracture. We have mainly focused our interest in the low speed regime of cracking when samples are in a corrosive environmental atmosphere [3] (e.g. in the presence of water molecules). For that reason it is crucial to investigate physical and chemical processes involved in this so-called

stress corrosion regime at the nanometer scale. Important questions such as i) the main characteristics of deformation processes at the vicinity of the crack tip, ii) the chemical nature and iii) the physical state (liquid or gaseous phase) of the aqueous medium at the vicinity of the crack tip have to be dealt with in order to better understand fundamental fracture mechanisms. For that purpose we have experimentally studied the low speed fracture regime ($10^{-3} - 10^{-10}$ m.s⁻¹ and below) for different glassy materials in a carefully mastered surrounding atmosphere. The chosen mechanical system enables us to work in pure tensile mode (mode I). By using an experimental set-up based on combined optical and atomic force (AFM) microscopy techniques we have characterised in *in-situ* and *real-time* conditions the fracture processes. In this talk several important results as obtained from our experiments will be discussed: - ductile-like behaviour ahead of the main crack 'tip' at a temperature far below the glass-transition one [4]; - local ionic migration processes [5]; - occurrence of non-equilibrium hydrous liquid condensate between the two fracture surfaces in the vicinity of the crack tip in gaseous atmosphere at elevated humidity [6]. [1] B. N. Cox, H. Gao, D. Gross and D. Ritter, J. Mech. Phys. Solids **53** (2005) 565. [2] B. Luan and M. Robins, Nature **435** (2005) 929. [3] J.-P. Guin and S.-M. Wiederhorn, J Non-Cryst. Solids **316** (2003) 12. [4] F. Célarié, S. Prades, D. Bonamy, L. Ferrero, E. Bouchaud, C. Guillot and C. Marlière, Phys. Rev. Letters **90** (2003) 075504. [5] F. Célarié, M. Ciccotti and C. Marlière, submitted. [6] L. Wondraczek, A. Dittmar, C. Oelgardt, M. Ciccotti, F. Célarié and C. Marlière, submitted.

2:00 PM *NN9.2

The Topography of Fracture Surfaces in Silicate Glasses.
Sheldon Martin Wiederhorn¹ and Jean-Pierre Guin¹; ¹National Institute of Standards and Technology, Gaithersburg, Maryland; ²National Institute of Standards and Technology, Gaithersburg, Maryland.

The topography of surfaces formed by subcritical crack growth was investigated using the atomic force microscope. Our objective was to determine how well the two fracture surfaces matched after being formed by cracks moving at slow velocities. Fracture surfaces in silicate glasses are known to be rough on the molecular scale. It is not known, however, if the roughness is left as a consequence of plastic deformation, or a chemical reaction that occurs during the fracture process. It is also not known if the character of the fracture surface roughness changes as a function of the crack growth rate and the glass composition. Crack growth experiments were performed on silica and soda-lime-silicate glasses, in air and water over a velocity range of 1e-10 m/s to 1e-2 m/s. The freshly fractured surfaces were then imaged by atomic force microscopy and the surfaces compared. Within experimental measurements, both surfaces were found to be nearly identical. Silica glass surfaces matched normal to the fracture plane to better than 0.3 nm for the entire range of experimental variables. Soda-lime-silicate glass surfaces matched to an accuracy of 0.5 nm to 0.8 nm normal to the fracture plane, depending on crack velocity. These results are consistent with the idea that the fracture of silicate glasses is a completely brittle process (no shear bands, no cavity formation). The surface roughness was found to decrease as the crack velocity for both glasses tested. These results are discussed with regard to those obtained for more rapidly moving cracks, for which roughness is found to increase with increasing crack velocity.

3:30 PM NN9.3

Nano-mechanisms of plasticity in semi-crystalline polymer films as revealed by in-situ Atomic Force Microscopy (AFM).
Vincent Ferreiro, Christophe Thomas and Ghislaine Coulon; CNRS, USTLille, Villeneuve d'Ascq, France.

In previous works, we have shown using Atomic Force Microscopy (AFM) that the nucleation and the propagation of shear bands within the amorphous phase are responsible of the yield point of polyamide 6 (PA6) films. This observation suggests that the amorphous phase governs the plasticity of semicrystalline polymers of low degree of crystallinity. As reported in the literature, the yielding of highly crystalline semicrystalline polymers is controlled by the crystalline phase through homogeneous shear of the crystalline lamellae via the nucleation and the propagation of screw dislocations. In the present study, we propose to investigate the competition between the amorphous phase and the crystalline one during the plastic deformation as a function of the degree of crystallinity. It is well known that, in amorphous polymers, two modes of deformations are observed: shear banding and crazing. It is thus expected that, for a given semicrystalline polymer showing a large range of degrees of crystallinity, mechanisms such as shear banding or crazing should be active at low degree and be replaced progressively by crystal slip as the degree of crystallinity increases. The plastic deformation behaviour of both Polybutene-1 (Pb-1) and Polycaprolactone (PCL) films has been investigated as a function of the degree of crystallinity. Depending on the crystallization conditions, these semicrystalline polymers exhibit a quite large range of degrees of crystallinity (70 % ≤

$\chi \leq 30\%$). AFM images have been recorded in the tapping mode TM. By analyzing the three different kinds of images: height, amplitude and phase ones, it has been possible to visualize and to characterize the nucleation and the propagation of the nanomechanisms of plasticity within both the amorphous phase and the crystalline one. A tensile-test apparatus has been designed in our laboratory in order to deform polymer films directly under the AFM head and to follow the evolution of the nanomechanisms as a function of time within the same area of the polymer film. The experiments have been performed for different strain rates and draw ratios. Preliminary works show that the yielding of Pb-1 films of low degree of crystallinity ($\chi \approx 40\%$) is controlled by the nucleation of shear bands within the amorphous phase. AFM in-situ observations show that the density of shear bands increases as a function of draw ratio. For high draw ratios, the shear bands propagate all over the sample and spherulites are entirely sheared. By crossing the lamellae, they form crystalline nanoblocks. For PCL films ($\chi \approx 40\%$), shear bands are also active but they are localized; fibrillation is observed within the shear bands. For highly crystalline Pb-1 films (65%), the yield point is governed by the crystalline phase through the built up of nanofibrils within the spherulites. In situ observations show that the thickness of the fibrils (50-100 nm thick) does not vary with the draw ratio.

3:45 PM NN9.4

AFM Studies of the Surface Relief Associated with Various in the Deformation Mechanisms in Metastable β Ti-Mo-Based Alloys. Lichun Zhang¹, Mark Aindow¹, S. P. Alpay¹ and Ming Wu²;

¹University of Connecticut, Storrs, CT, Connecticut; ²Memry Corporation, Bethel, Connecticut.

Atomic force microscopy (AFM) is proving to be an extremely powerful analytical tool for the observation of the subtle surface relief that accompanies certain deformation micromechanisms. When used in combination with transmission electron microscopy (TEM), AFM offers unique opportunities for experimental investigations on the crystallography of deformation bands. In this study we have used this combined AFM/TEM approach to investigate the deformation behaviors of metastable β Ti-based alloys, which depend strongly on both the alloy compositions and the thermal history. A remarkable variety of deformation mechanisms was observed: these include stress-induced formation of martensitic phases, planar dislocation glide and {332} deformation twinning. The topographic features that arise for each of the deformation modes have been revealed using AFM. These data have been used to determine the magnitudes of the shears associated with each process. The surface relief observed for dislocation glide and stress-induced martensite corresponds closely with what one would expect from geometric models. For {332} deformation twinning, however, the relief implies a much larger shear than one would expect on the basis of existing models. A new model for {332} twinning is proposed which both accounts for the measured shears and helps to explain the pseudoelastic limit in these alloys.

4:00 PM NN9.5

Radial elasticity of multiwalled carbon nanotubes. Ismael Palaci², Stephan Fedrigo², Harald Brune², Christian Klinke³, Michael Chen¹ and Elisa Riedo¹; ¹Physics, Georgia Institute of Technology, Atlanta, Georgia; ²EPFL, Lausanne, Switzerland; ³IBM Corp, Thomas J Watson Res Ctr, Yorktown Hts, New York.

The exceptional mechanical, electrical, and thermal properties of carbon nanotubes (CNTs) have attracted great scientific and technological interest. CNTs have cylindrical symmetry with axial mechanical properties characterized by the strong in plane covalent C-C bond. The strength of this bond gives rise to an extraordinary axial stiffness, as pointed out by several experimental and theoretical studies finding values for the axial Young modulus of about 1 TPa. In graphite, the C11 in plane elastic constant is 1.06 TPa, while the perpendicular elastic constant C33 is only 36 GPa. Similarly the radial Young modulus of CNTs is expected to be much smaller than the axial one. Evidence for the softness of CNTs in the radial direction has been reported in experiments under hydrostatic pressure, where a critical pressure of only 2 GPa has led to the collapse of single-walled CNTs with a radius of 0.7 nm. Achieving a fundamental understanding of the radial deformability of CNTs is important for applying them in nanoelectromechanical and nanoelectronic systems. For example, the radial deformation of CNTs may strongly affect their electrical properties. However, our quantitative understanding of the radial elasticity of CNTs is so far based on studies performed on only one tube, with an unknown number of layers, and using deformations up to the nonlinear regime. Here, we present quantitative measurements of the radial elasticity of 40 multiwalled CNTs with external radii ranging from 0.2 to 12 nm and having a constant ratio of external to internal radii of $R_{ext}/R_{int} = 2$ nm [1]. We underline that the NT with $R_{ext} = 0.2$ nm is most likely a single-walled NT. By means of modulated nanoindentation with an AFM, we find that the radial stiffness strongly increases with decreasing external diameter. The radial Young modulus E_{rad} is extracted from the experimental

results by applying the Hertz model. E_{rad} is found to decrease to an asymptotic value of 30 GPa for larger tube sizes. We also perform molecular dynamics simulations with empirical C-C potentials to mimic the experiments and shed some light on the applicability of the Hertz theory in this context. Force-indentation curves obtained by the simulations indicate a similar trend in E_{rad} (Rext). [1] I. Palaci et al. Physical Review Letters, 94 175502 (2005)

4:15 PM NN9.6

Fabrication and Evaluation of Ultrananocrystalline Diamond and Tetrahedral Amorphous Carbon Atomic Force Microscopy Probes. Guoqing Ning¹, Anirudha V. Sumant¹,

Grierson David¹, Jennifer Gerbi², Orlando Auciello², James Birrell², Xingcheng Xiao², John A. Carlisle², Tom Friedmann³, J.P. Sullivan³ and Robert Carpick¹; ¹Engineering Physics Department, Univ. of Wisconsin, Madison, Madison, Wisconsin; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Nanostructure Physics, Sandia National Laboratory, Albuquerque, New Mexico.

Minimizing wear on tips used in atomic force microscopy (AFM) is a critical challenge. Ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C) have excellent mechanical and tribological properties that are ideally suitable for SPM probes, such as low macro-scale wear and friction, high hardness, and chemical inertness. In this presentation we report the first successful batch fabrication of monolithic probes from both materials. An array of pyramidal etch pit molds were formed on a silicon wafer by anisotropic etching in KOH. Oxidation sharpening of the molds was performed, followed by deposition of UNCD or ta-C films 1-3 um thick. The coated wafers were then subjected to metal mask deposition, photolithography, and oxygen reactive ion etching to form monolithic cantilevers with integrated pyramidal tips. Individual probes were then released and physically bonded to a holding substrate for testing. SEM, TEM and AFM have been used to evaluate the probes. SEM images show no significant bending of the cantilevers after release, indicating low residual stress, and no stiction between the cantilever and the surface below, which is indicative of the low adhesion energies and hydrophobicity of the UNCD and ta-C surfaces. TEM was used to characterize the apex radius of the tip. We discuss the benefits of oxide sharpening of the silicon molds, without which the tips often form rather large radii above 200 nm. The cantilevers were mounted in an AFM to measure the resonant frequency and quality factor of the probes. From this, the spring constant and Young's modulus have been calculated and compare favorably with the moduli measured previously on these films using other techniques. Furthermore, the UNCD and ta-C AFM probes have been successfully used to image samples in contact mode and high quality topographic and friction images have been repeatedly obtained without noticeable degradation of the image quality. We will discuss how the rate of wear of these tips compares to silicon and silicon nitride probes under the same loading conditions. *Part of this work was supported by the US Department of Energy, BES-Materials Sciences, under Contract DE-FG02-02ER46016, and the Air Force Office of Scientific Research under Contract FA9550-05-1-0204. *Part of this work was funded by Sandia. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:30 PM NN9.7

An AFM-Based Scanning Method for Mechanical Testing of Nanoscale Cantilevers. Peter J. Ryan^{1,2}, George G. Adams¹, Nicol

E. McGruer² and Sinan Muftu¹; ¹Mechanical and Industrial Engineering, 334 SN, Northeastern University, Boston, Massachusetts; ²Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts.

In this investigation, nanomechanical cantilever test structures were fabricated from Chromium. A method was developed, using an Atomic Force Microscope (AFM), for mechanical testing by scanning these structures under different levels of loading. The resulting data allowed the mechanical properties to be deduced. Future investigations should enable smaller structures (cantilevers and bridges) to be fabricated and tested with a variety of test materials. Mechanical characterization of materials has been an essential step in the design of a great variety of macro-scale devices used in industry and by consumers. However material behavior at the micro- and nano-scales is known to differ significantly from the macro-scale. As technology moves toward producing products that operate at ever smaller length scales, there exists a need to develop new methods of mechanical testing at these extremely small scales. Current methods include two classes - test beds consisting of fabricated devices integrated with testing instruments (such as MEMS devices), and instruments such as micro- and nano-indenters in which the mechanical tester is separate from the material to be tested. The first class has practical as well as materials limitations, whereas the second class allows for better versatility but is limited to measurements of properties at the surface

of the material. An array of nanoscale Chromium test cantilever structures (each 50 nm x 150 nm x 10 μ m) was fabricated. Consistency and uniformity of these structures, which is essential for an accurate determination of mechanical properties, depends strongly on the process type and processing parameters. It was found that better uniformity was obtained using a positive e-beam resist process, rather than a negative e-beam resist process. Following fabrication of these devices, a method was developed for mechanical testing of these structures using an AFM. A pre-calibrated AFM tip was used to scan the test cantilever in contact mode. Several scans along the length of each nano-cantilever, starting from the fixed end, were performed under different values of the applied load. Although the nanostructures exhibited significant residual curl, the measurements under different values of the load allowed these residual displacements to be compensated for. Note that with a constant load applied to the test cantilever, the bending moment at any cross-section continually increases as the AFM scans from the fixed toward the free end. Also because each cantilever cross-section is subjected to a bending moment, the stress- and strain-gradients within each nanometer scale cross-section are quite large. These strain-gradients affect mechanical behavior differently than does a uniform strain. The acquired data was then used to construct a stress-strain curve. These results gave a value of 80 GPa for the Young's Modulus which is significantly less than the thin-film value of 140 GPa and the bulk value of 248 GPa.

4:45 PM NN9.8

A Novel Approach to Evaluation of Elastic Modulus of Hard and Superhard Materials Using SPM. Alexey S. Useinov and Kirill V. Gogolinskiy; Scanning Probe Microscopy, Technological Institute for Superhard and Novel Carbon Materials, Troitsk, Russian Federation.

Materials which have hardness exceeding 25 GPa and elastic modulus exceeding 400 GPa are usually referred as hard and superhard materials. Measuring the elastic properties of such materials is always accompanied with a number of difficulties. The only appropriate method for mechanical properties investigation on a nanometer scale is the contact method. It is based on the analysis of interaction between very sharp tip (indenter) and material surface. The main techniques which use contact method are scanning probe microscopy and nanoindentation. Standard SPMs are not applied for investigation of hard materials, since they use rather soft cantilevers and tips usually made of silicon. Basely they are used for investigation of soft polymers and metals. Standard nanoindentation method has not enough spatial resolution (micron and worse) to investigate nanosized objects. Besides, it gives statistically proper result when tip penetrates inside the material for the depth of 30-50 nm and more. The measurements using ultra low loads usually lead to overestimation of the measured values. Furthermore, the standard model (Oliver-Pharr) does not count for such effects as pile ups which also are supposed to have significant influence. Besides, in this method the material is supposed to be plastically deformed, which is hardly accessible for hard materials. A novel method of the quantitative non-destructive elastic modulus evaluation has been proposed. The method is based on the scanning probe microscope "NanoScan" operating in oscillating resonant mode. The main specialty of the "NanoScan" is the use of the probe with unusually high spring constant of the cantilever (10^4 - 10^5 N/m) and the possibility to use diamond tips or tips made of ultrahard fullerite C₆₀. The oscillating tip is pushed against the surface, causing the probe resonant frequency to change. The elastic modulus evaluation is based on measuring and analyzing the dependency of frequency shift from the tip penetration into the sample surface. This method allows measuring elastic modulus in the range from 10 up to 1100 GPa which corresponds to the materials from hard polymers up to diamond. The advantage of this method is high locality. It can be used for investigation of small features on the surface with size down to 50-100 nm, making possible characterization of separate phases in multiphase and composite materials. This method is also effective for measuring elastic modulus of thin films (150 nm and more), as the penetration of the tip into the surface is only 10-15 nm and the contact is absolutely elastic, i.e. no plastic deformation occurs. The method have shown good agreement with common nanoindentation method for smooth homogeneous surfaces. At the same time it has several apparent benefits for investigation of hard and superhard materials, multiphase and composite materials and thin films.

SESSION NN10: Poster Session: Scanning Probe
Microscopy in Materials Research
Chair: Ernst Meyer
Wednesday Evening, November 30, 2005
8:00 PM
Exhibition Hall D (Hynes)

NN10.1

Local Deposition of Nano-sized Liquid Droplet from an

Ultrasml Aperture on an AFM Tip. Kiyohiro Kaisei¹, Nobuo Satoh¹, Kei Kobayashi², Kazumi Matsumige^{1,2} and Hirofumi Yamada^{1,3}; ¹Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; ²International Innovation Center, Kyoto University, Kyoto, Japan; ³Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Kyoto, Japan.

Local deposition techniques based on scanning probe methods such as the dip-pen lithography and the AFM stencil method have remarkable advantages over the normal lithography process in terms of simplicity and applicability. In particular, since most of the organic films cannot be patterned by the conventional lithography method using polymer resist films, these techniques are greatly useful for the patterning process of organic materials including biomolecules. In this paper we describe a novel deposition method for liquid droplet with the size below a few hundred nanometers using a microfabricated AFM cantilever. Droplets were ejected onto a substrate surface from an aperture, made at the apex of the probe tip of the cantilever by applying high electric field between the tip and the substrate. A commercially available silicon nitride (SiN) cantilever with a hollow-pyramidal tip was used. The backside was coated with Au. We used two types of the cantilevers having spring constants of 0.1 N/m or 15 N/m. A 200-nm-wide aperture was made at the very end of the probe tip by focused-ion-beam milling (FIB). A solution droplet with the size of about 20 microns was put at the back of the tip of an AFM cantilever. In order to keep the droplet in the "reservoir" region at the backside of the tip area we chemically modified the Au-covered cantilever surface by depositing self-assembled monolayer (SAM) films such that the reservoir area and the other area were hydrophilic and hydrophobic, respectively. We first formed an Fmoc-aminoalcanol SAM film on the entire backside of the cantilever and then removed the film selectively only on the "reservoir" region by UV irradiation through a photomask. Finally the bare Au area was the hydrophilic region working as the solution reservoir while the other area was hydrophobic due to the hydrophobic property of the end of the Fmoc molecule. When a high electric field exceeding 10 kV/m was applied between the cantilever and the substrate, the droplet was ejected to the substrate. The deposited surface was imaged by the same cantilever. Furthermore, patterning process was carried out by vector-scanning of the aperture.

NN10.2

Nanolithography on SiO₂/Si(111) substrate using ultra high vacuum scanning tunneling microscope. Shigeya Naritsuka^{1,2},

Etsuko Hosoda¹, Chisa Yoshida¹, Yasuyuki Kawamura¹, Hyungjin Bang², Hideaki Uemura², Yuka Ito² and Takahiro Maruyama^{1,2};
¹Materials Science and Engineering, Meijo University, Nagoya, Japan;
²21st Century COE program, Meijo University, Nagoya, Japan.

Lithography with scanning tunnel microscope (STM) is very promising technique to realize nano-scale patterning for nano fabrications. We have already reported a successful result about nano-lithography on SiO₂/Si substrate using ultra high vacuum scanning tunneling microscopy (UHV-STM)[1]. In this report we discuss the mechanism of STM lithography with comparing experimental results and simulations. 1x7x0.3 mm³ size-cut n-type Si (111) was used as a substrate. 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 removal of the surface native oxide by flashing at 1200°C for 15 seconds, a thin oxidation layer was formed by heating the substrate at 930°C for 15 minutes, in an atmosphere of oxygen with the pressure of 1x10⁻³ Pa. For the lithography, bias voltage, tunneling current and moving velocity of tip were varied between 75-150 eV, 3-10 nA and 0.47-1.6 nm/s, respectively. Surface post-observation was performed with bias voltage and tunneling current with range of 2.0-4.3 eV and 0.05-0.3 nA. Numerical simulation was also performed to find out how the electron beam from the STM tip would extend over the surface of the substrate. In the simulation, the current density on the surface of a tip was given by the Fowler-Nordheim equation. Nano-size lines, whose width varied from 24 nm to more than 100 nm, were successfully patterned on thermally formed Si oxide on Si (111) substrate. The width increased with tunneling current and decreased with moving velocity of the tip. But, the bias voltage showed only a slight influence on the width. Comparing the experimental width of lithography and the simulated distributions of the current density, the threshold current density for lithography was investigated. Consequently, it was found that the lithography largely depends on the peak current density passed through the position. The detailed mechanism of the lithography will also be discussed. [1] H. Bang et al., Abstract of 2004 MRS fall meeting, C5.12.

NN10.3

Local Characterization of Ultra-Thin HfO₂ by *in-situ* Ultrahigh Vacuum Scanning Tunneling Microscopy.

Lei Wang, Kun Xue and Jian-bin Xu; Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

HfO₂ and Hf silicates are emerging as promising oxides to potentially replace SiO₂ as the gate dielectric material for future complementary metal oxide semiconductor (CMOS) technology. [1] In this work, we use ultrahigh vacuum scanning tunneling microscopy (UHV-STM) to *in situ* characterize ultra-thin HfO₂ on silicon substrate. Samples were prepared by ultra-high vacuum e-beam evaporation of Hf atoms and simultaneous oxidation on Si(111). The film thickness was varied from less than one monolayer to a few monolayers. It is found that the hafnium oxide and/or silicate species first appear as clusters after deposition, and then migrate to the silicon surface to form individual islands. UHV post-annealing was *in situ* conducted at different temperatures, and the morphology alteration was subsequently analyzed. Local electrical properties such as current-voltage (I-V) and dI/dV characteristics were performed on a nanometer scale. The correlation between the STM images and the fixed charges in the oxides for both annealed and as-grown samples has been found [2]. Reference: [1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. 89, 5243 (2001). [2] N. Miyata et al., Appl. Phys. Lett. 86, 112906 (2005).

NN10.4

Polarized Guide-Collection-Mode Near-Field Scanning Optical Microscopy. Tadashi Mitsui, Kazuaki Sakoda and Giyuu Kido; Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Japan.

We fabricated original probes for the near-field scanning optical microscopy (NSOM) with polarization-preserving optical fibers, and successfully observed the polarization properties of propagation light within a polymeric optical waveguide by separating independent polarization components. The polarized NSOM technique revealed that the periodic intensity modulation along the waveguide axis has a polarization property whose electric vector is perpendicular to the waveguide axis, and that the period of intensity modulation nearly equals the wavelength inside the waveguide. The intensity modulation originates from a standing wave caused by a resonator formed between the entrance and exit facets. In addition, in order to characterize the influences of defects and weak stresses within a polymeric optical waveguide, the author intentionally printed an indentation in the vicinity of the waveguide, then evaluated the resulting influences using polarized guide-collection-mode NSOM images taken around the indentation. When transverse magnetic polarized light enters a waveguide, the light intensity becomes greater on the near side of the indentation than on the far side, as measured by a linearly polarized component perpendicular to the direction of light propagation. The most probable cause of this phenomenon is microdefects generated by the printing of the indentation. The polarized NSOM technique is useful in searching for small defects or stresses within integrated photonic devices.

NN10.5

Abstract Withdrawn

NN10.6

The extended two-parameters AFM spectroscopy. Valery Prokhorov, Sergey Saunin and Victor Bykov; NT-MDT, Moscow, Russian Federation.

The procedure called two-parameters AFM spectroscopy in which a set of amplitude-frequency A(f) curves of oscillating cantilever mode is acquired at a continuous change in a piezo-position (z) has been developed. The result is presented as two-dimensional A(f,z) pattern (map) in the (f,z) space with color corresponding to the oscillation amplitude. Areas corresponding to the attraction (A) and the repulsion (R) regimes of probe-surface interactions are clearly distinctive in such patterns as domains with different slopes of lines of a constant amplitude which additionally may have jumps on domain borderlines. Three types of such domains called A1, A2, R may be generally observed (Fig.1). A(f,z) maps essentially depend on a number of parameters: the cantilever spring constant and driving amplitude, the surface force fields and the direction of frequency sweep (hysteresis). At low driving amplitude only A1 and A2 domains exist, its increase results in appearance of R-domain, which competes with A2 domain and completely displaces it at high amplitudes. The procedure extends common A(f) and A(z) spectroscopies used in AFM devices and monitors in a convenient visual way the complex picture of cantilever dynamics and tip-surface interactions. In practice it may be used at optimization of scanning parameters to avoid instabilities.

NN10.7

The AFM visualization of polyolefins molecules on mica and HOPG. Valery Prokhorov, Sergey Saunin, Andrey Shubin and Victor Bykov; NT-MDT, Moscow, Russian Federation.

Molecular size compact nanoobjects with a height within 1-5 nm as well as isolated lamellae and thin lamellar layers were formed on mica and HOPG by depositions at temperatures within 20-150°C from diluted solutions of semicrystalline polyolefins such as polyethylene, isotactic polypropylene and their copolymers and characterized by AFM with a high resolution. A large variety of polymer surface conformations is observed: isolated lamellae and epitaxial lamellar domains, nanocrystallites, networks and tangled coils. As a general conclusion: mica favors the formation of nanocrystallites whereas depositions on HOPG result in a formation of lamellar structures. The lamellae both isolated and in lamellar domains obtained at high-temperature depositions both on mica and HOPG revealed longitudinal undulations attributed to a manifestation of intralamellar chain tilt. For low-temperature depositions three lamellae types with no undulations were observed on HOPG differed by a morphology, long period and azimuthal orientation. Nanocrystallites (NC) were typically observed at depositions on mica. They have regular geometrical shapes both simple rectangular and more complex. The high-resolution height and phase AFM images clearly differentiate the central crystalline core and the amorphous fold periphery within NC indicating the lamellar-type packing. Of two lateral NC dimensions the first one was found to be in the range of 7-16 nm and is associated with a polymer fold length whereas the second may vary greatly from several nm-s to tens nm-s due to a large variation in a number of folds of polymer chain(s) forming the nanocrystallite. The NC height histograms show sharp peaks separated by a step of about 0.5 nm indicating layer-by-layer chain packing. Two different NC morphologies were observed: smaller (predominantly single-molecule) platelets of 0.5-2.5 nm in a height with flat tops and relatively long NC with a transversal blocky substructure with a different height of constituent blocks within 2-5 nm. In some cases extended polymer networks were observed in which NC located in junctions are connected with each other by stretched polymer chains. The length distribution of stretched chain segments decays exponentially with a characteristic length of 30-50 nm, the size of crystalline junctions varied greatly with least dimensions corresponding most probably to two polymer molecules inside. Most unexpected was the observation on mica of polymer molecules in a coiled surface conformation [1]. The coils have both highly tangled sites and extended straight segments of 5-15 nm in a length much larger than the persistence length of 1 nm. The coils mobility is essentially frozen on a surface implying the action of some stabilization mechanism. The model of such stabilization is discussed based on the existence of salt layer on mica surface in which polymer molecules are embedded. [1] V.V.Prokhorov, K.Nitta, M.Terano, Macromol. Chem. Phys. 2004, 205, 179-186.

NN10.8

Probe Processing for Atomic Force Microscopy and Spectroscopy Applications. A. L. D. Moreau¹, D. B. Nakabayashi^{2,1}, K. Vicaro¹, A. von Zuben¹, C. S. Lambert¹, P. Silva², D. M. Ugarte^{1,2} and M. A. Cotta¹; ¹UNICAMP - Instituto de Física Gleb Wataghin - DFA, Campinas, SP, Brazil; ²Laboratório Nacional de Luz Síncrotron - LME, Campinas, SP, Brazil.

Atomic Force Microscopy (AFM) has shown to be a powerful tool for probing intermolecular interactions because it can resolve forces with piconewton sensitivity with nanometer-size spatial resolution. One limitation factor of AFM, however, is associated to probe size and aspect ratio. We show here results on probe functionalization and welding to carbon-nanotubes with the aid of a nanomanipulator inside a Field Emission Gun-Scanning Electron Microscope. Commercial Si tips were metalized and functionalized with mercaptoundecanoic acid (HS(CH₂)₁₀COOH). The metallization process was carried out in order to use the strong S-Au bonds that thiols naturally form on Au surface. Si tips coated with Cr/Au films deposited by thermal deposition or with Pt/Au films by sputtering techniques were analyzed using SEM. The stability of the metal films thus produced is analyzed in terms of wear due to sample-tip approach conditions and number of adhesion measurements. Our results show that the sputtered films provided more stable tips, if the best set of parameters controlling tip/sample approach are used for the measurement. For the COOH thiol-functionalized tips tested with Au-coated substrates functionalized with the same procedure, adhesion forces approximately 5 times larger than van der Waals forces were measured. The statistical dispersion of tip radius-normalized adhesion force values was correlated to the tip integrity analyzed by SEM. On the other hand, in order to improve the AFM spatial resolution, we have assembled multiwalled carbon nanotube (diameter 30nm) on commercial Si probes with a nanomanipulator inside a FEG-SEM. AFM images have been carried out in semiconductor quantum dot samples; a clear improvement of the resolution with CNT's probes with regard to conventional probes was obtained. The best results in terms of imaging and tip wear were observed for short CNT probes encapsulated with a thin cap of carbon-related material.

NN10.9

Near-field Light Detection by Dissipative Force Modulation

Method in FM-DFM using a PZT Cantilever. Nobuo Satoh¹, Takeshi Fukuma¹, Kei Kobayashi², Shunji Watanabe³, Toru Fujii³, Kazujmi Matsushige^{1,2} and Hirofumi Yamada^{1,4}; ¹Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; ²International Innovation Center, Kyoto University, Kyoto, Japan; ³Nikon Corporation, Sagami-hara, Japan; ⁴Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Kyoto, Japan.

Scanning near-field optical microscopy (SNOM) has been a powerful tool not only for imaging surface topography but also for investigating optical properties at a nanometer-scale resolution. However, low light intensity detected in SNOM remains a major problem related to the limit of the spatial resolution. In this paper we describe a new method for near-field light detection by a highly sensitive force-sensing technique in dynamic force microscopy (DFM) using frequency modulation (FM) detection. The interaction forces measured by DFM using FM detection are classified into two categories; conservative and dissipative forces. The conservative forces induce a frequency shift of the cantilever resonance while the dissipative forces cause an amplitude variation of the cantilever oscillation. It was recently shown that the use of the dissipative force detection in DFM significantly increased the force sensitivity [1]. The technique, referred to as dissipative force modulation (DM) method, was applied to Kelvin-probe force microscopy (KFM), which showed that the dissipative force detection (DM-KFM) was about ten times better than the conservative force detection (normal KFM) in the force sensitivity. We applied the DM method to SNOM (DM-SNOM), where the modulation frequency of the laser light was tuned to the oscillation frequency of the cantilever. When the probe tip was brought into close proximity to a sample surface with evanescent field generated by laser light illumination in a total-internal-reflection setup, the near-field light can be detected as the light-induced amplitude modulation of the dissipative force. Possible origins of photo-induced forces detected here can be photo-thermal effect, optical pressure, or electrostatic force, which have not been assigned yet. We used two samples: one was a glass substrate with a Cr mask pattern and the other was an ITO/glass substrate on which gold nanorods were deposited. The envelope of the modulated laser light was also modulated at a frequency of 2 kHz for the lock-in detection in the DM method. We used batch-fabricate lead zirconate titanate (PZT) piezoelectric cantilevers because they also worked as a sensor in SNOM. Thus, the images obtained by the DM method were directly compared to the corresponding SNOM images. We have succeeded in obtaining photo-induced images of the samples by DM-SNOM. The obtained images were consistent with the corresponding SNOM images apart from some faint undulation in contrast, which appeared only in the SNOM images. Since the contrast undulation probably originated from the interference effect of some far-field stray light accidentally detected by the photo detector, the photo induced signal in DM-SNOM was not affected by the far field light. Reference [1] Takeshi Fukuma, Kei Kobayashi, Hirofumi Yamada, and Kazumi Matsushige, Rev. Sci. Instrum., 75 (2004) 4589.

NN10.10
Modeling the mechanical interactions between ligands and cell-bound receptors. Emily Walton and Krystyn J. Van Vliet; Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Binding events between ligands and receptors on cell surfaces control many important biological processes, including signaling cascades, intercellular drug responses, cell adhesion, and cell migration. Since the first atomic force microscope experiments measured adhesion forces between individual ligand-receptor pairs in 1994, there has been a large experimental effort toward use of nanomechanical force to quantify the binding kinetics between these receptors and their respective ligands and to map molecular receptors on living cell surfaces. Although the requisite experimental capabilities have developed rapidly, interpretation of experimental results at these force and length scales is limited by analytical models that assume both molecules to be bound to rigid substrates. These models may well approximate atomic force microscope experiments for which the receptor is bound to a rigid substrate and the ligand is bound to the AFM cantilever, but do not recapitulate ligand-receptor interactions on mechanically compliant and structurally dynamic living cells. We will present results from classical molecular dynamics and multi-scale hybrid computer simulations designed to address the lack of an appropriate model for interpreting nanomechanical force measurements of ligand-receptor binding on living cell surfaces, including archetypal binding partners such as biotin-streptavidin against which considerable experimental results can be compared.

NN10.11
Observation of piezo(ferro)electricity in a confined crystallite. Pradyumna Narain Gupta¹, Sergei Kalinin², Himanshu Jain¹, David Williams¹, J. Shin² and A. Baddorf²; ¹Materials Science and Engg.,

Lehigh University, Bethlehem, Pennsylvania; ²Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Transparent ferroelectric glass-ceramics (TFGC) are being developed as an inexpensive and easy to fabricate alternatives for nonlinear optical materials such as LiNbO₃ single crystal. The development of the ferroelectric phase inside the confining glass matrix is the key issue in TFGC because the ferroelectric phase is responsible for the nonlinear optical activity of the material. LaBGeO₅ (LBGO) is a model material for fundamental studies because of its ability to transform into ferroelectric phase from the glass phase without changing its composition. Bulk crystallized TFGC are successfully prepared through two-step heat treatment of the LBGO glass. A series of samples with several sizes of the crystallites are produced. To monitor the development of the ferroelectricity of the crystallites, piezoresponse force microscopy (PFM) is performed to image the ferroelectric properties of clamped LBGO crystallites on the nanoscale level. Also, a method has been outlined to extract the piezoelectric response of the crystallites from the orientation map obtained from Electron Backscattered Diffraction (EBSD) microscopy.

NN10.12
An In-situ and Real-Time Biodegradation Study of Thin Films of Polyhydroxyalkanoate Polymers Using Atomic Force Microscopy. Brian H Augustine¹, Stuart S. Williams¹, Patrick L. Turner¹ and Stephen M. Baron²; ¹Department of Chemistry, James Madison University, Harrisonburg, Virginia; ²Department of Biology, Bridgewater College, Bridgewater, Virginia.

In-situ and real-time atomic force microscopy (AFM) was used to monitor the enzymatic biodegradation of patterned samples of polyhydroxyalkanoate (PHA) thin films deposited onto gold substrates. Poly 3-hydroxybutyrate-co-poly 3-hydroxyvalerate [P(3HB-3HV)] thin films were prepared by the selective dewetting of soft lithographically patterned gold substrates with feature sizes down to 10 μm . The samples were then exposed to an enzyme solution containing 20 μL of Tris-Cl buffer solution and 20 μL concentrated enzyme solution produced from *Streptomyces* sp. bacterium. The liquid cell capability of the AFM allowed for the monitoring both in-situ and in real-time the biodegradation process. The data collected was then externally analyzed by comparing changes in surface area with time to measure a degradation rate. Damage to the surface microstructure was also intentionally created using the nanomanipulator capability of the AFM to dramatically increase the biodegradation rate. We will discuss the probe forces required to increase the biodegradation process and the model to explain this phenomena.

NN10.13
Abstract Withdrawn

NN10.14
Atomic Force Microscopic Studies on Microphase-Separated Structure of Polyurethane Elastomers. Mutsuhisa Furukawa, So Kugumiya and Ken Kojo; Materials Science and Engineering, Nagasaki University, Nagasaki, Japan.

Polyurethanes are composed of a rigid hard segment and flexible soft segment, and the microphase-separated structure formed with both segments is closely related to their properties. Although tremendous numbers of study have done for evaluation of the microphase-separated structure of the polyurethanes, there are no complete studies to observe the microphase-separated structure directly on account of their fine and complicated structure. In this study, we tried to observe the microphase-separated structure of the polyurethane elastomers (PUEs) with an atomic force microscopy (AFM). PUEs with different hard segment contents, 34 and 46 wt%, were prepared with poly(oxytetramethylene)glycol (PTMG), 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) by a prepolymer method. Microphase separation of the PUEs was investigated using Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimeter (DSC), small angle X-ray scattering (SAXS) and AFM. FT-IR and DSC measurements revealed that the degree of microphase separation for these PUEs became stronger with increasing hard segment contents. The hard segment domains, which were surrounded by the soft segment matrix, were clearly observed for the 34 wt% PUE. In contrast, spherulites whose diameter is ca. 5 μm were clearly observed for the 46 wt% PUE. Furthermore, a lot of small hard segment domains were observed in the spherulite region, indicating spherulites include much amount of hard segment component. The difference in the microphase-separated structure at local area was firstly confirmed by AFM observation.

NN10.15
Local Scale Correlations Between Adhesion Hysteresis And Friction. Robert Szoszkiewicz¹, Bharat Bhushan², Bryan D. Huey³,

Andrzej J. Kulik⁴ and Gerard Gremaud⁴; ¹Physics, Georgia Institute of Technology, Atlanta, Georgia; ²Ohio State University, Columbus, Ohio; ³University of Connecticut, Storrs, Connecticut; ⁴EPFL, Lausanne, Switzerland.

Adhesion hysteresis is the difference between the work necessary for separating two surfaces and that gained on bringing them back together. At local scales neither static methods like force-distance curves nor most of dynamic measurements cannot be implemented to probe adhesion hysteresis at the nanometer lengths and to date there are only a few reported studies. One is based on sub-nanometer NC AFM [1], while the other applies ultrasonic force microscopy (UFM) [2, 3] and is used here. It is interesting to study not only adhesion hysteresis, but also its correlation with friction forces. This relationship sets the ultimate resolution for local-scale friction, because adhesion hysteresis measurements are constrained only by the initial area of the tip-sample contact and do not require any lateral displacements as in typical friction experiments. The present work extends the relationship between adhesion hysteresis and friction towards molecular scales. These relationships are investigated theoretically and experimentally. We derive the analytical relations assuming an adhesive, elastic, and wearless tip-sample contact as well as the impact of a nanoscale roughness. We correct the model for nanoscale roughness by assuming the surface as fractal like at small scales. We validate our theoretical results through the adhesion hysteresis and friction measurements on a wide range of samples varying in their elastic and adhesive properties. [1] P. M. Hoffmann et al., Phys. Rev. Lett. 87 (2001) 265502. [2] R. Szoszkiewicz et al., J. Chem. Phys. 122 (2005) 144708. [3] R. Szoszkiewicz et al., J. Chem. Phys. 122 (2005) 134706.

NN10.16

Intermolecular Force Distribution in Nanocrystalline Diamond Film Measured using Atomic Force Microscopy for MEMS Applications. Sanju Gupta¹, R. J. Patel¹, G. P. Vierkant¹, J. T. Riley¹, P. W. May² and R. E. Giedd¹; ¹Physics and Materials Science, Missouri State University, Springfield, Missouri; ²Chemistry, Bristol University, Bristol, United Kingdom.

Carbon in its various forms, specifically diamond, may become a key material for the manufacturing of micro-electromechanical and nano-electromechanical (MEMS/NEMS) devices in the 21st Century [1-3]. The novel nanocrystalline diamond films may provide a basis for the revolutionary MEMS and NEMS [1]. Nevertheless, in order to effectively utilizing these materials for the abovementioned applications, understanding of their structural and physical (mechanical properties, in particular) become indispensable. The nanocrystalline diamond films were grown using hot-filament and microwave chemical vapor deposition techniques involving novel CH₄/doping in high hydrogen dilution and CH₄/Ar chemistry, respectively. Such physico-chemical processes induce synthesis-specific nanostructuring (grain size ranging 10-30 nm and a range sp³ versus sp² bonded C configurations) and offer several unique physical properties (extremely smooth surfaces, high electrical conductivity especially when doped with n- and p-type impurities) enabling them for several uses. In order to investigate intermolecular forces on these surfaces, the films were characterized extensively using atomic force microscopy in terms of topography (or height), force curves and force volume where the latter measuring elasticity maps. Traditional force curve measures the force felt by the tip as it approaches and retracts from a point on the sample surface, while force volume is an array of force curves over an extended range of sample area. Moreover, by using atomic force microscopy for nanoscale force constant measurements and surface spectroscopy techniques for detailed chemical and structural studies, we are able to demonstrate that the carbon bonding configuration (sp² versus sp³ hybridization) and surface chemical termination in both the undoped and doped nanocrystalline diamond surfaces has a strong effect on nanoscale intermolecular forces. The information in the force volume measurement was decoupled from topographic data to offer new insight into the materials and surface properties. These measurements are also complemented through X-ray diffraction and Raman spectroscopy techniques revealing their structure, bonding configurations, and residual stresses, for instance. We will present these results and discuss their potential impact for nano- and micro-scale applications. [1] A. Krauss, O. Auciello D. Gruen, A. Jayatissa, A. Sumant, J. Tucek, D. Macini, M. Molodvan, A. Erdemir, D. Ersoy, M. Gardos, H. Busmann, E. Meyer, M. Ding, Diamond and Related Materials, 10, No. 11, 1952 (2001). [2] H. D. Espinosa et. al. Mater. Res. Soc. Symp. Proc. Xx (2003). [3] A. V. Sumant, D. S. Grierson, J. E. Gerbi, J. Birrell, U. D. Lanke, O. Auciello, J. A. Carlisle, and R. W. Carpick, Adv. Mat., in press (2004).

NN10.17

Mapping the Electroluminescence of Semiconductors by Tapping-mode Conductive Atomic Force Microscopy. Manuel J. Romero, Chun-Sheng Jiang, Helio R. Moutinho and

Mowafak M. Al-Jassim; National Renewable Energy Laboratory, Golden, Colorado.

Recent developments in scanning probe microscopy (SPM) instrumentation are considerably expanding its potential to incorporate local measurements of multiple properties in different modes of operation. Nanostructures might be successfully applied in future generations of photovoltaics where innovative concepts for energy conversion can be explored and implemented. Fulfilling this vision will require the development of an entire next generation of SPMs to meet the ever-increasing demands imposed on our tools. In this contribution, we present the development of a tapping-mode conductive atomic force microscopy (AFM) for the mapping of the electroluminescence (EL) in the nanoscale. For these measurements, the optical feedback control commonly used in AFM is obviously detrimental because of the laser interference with the detection of EL. Furthermore, the conventional scanning head -which contains the piezo-scanner, laser, alignment optics, and split photodiode- makes it very difficult to project an efficient optical system for the detection of EL in reflection mode, which is best suited for most applications. We use a non-optical feedback control instead. The force sensor is based on a self-sensing and -actuating piezoelectric tuning fork and conducting tip. This sensor is very compact and allows very efficient detection optics for EL. The use of a tuning fork to monitor the cantilever deflection excludes the operation in contact -also referred to as static- AFM: dynamic operation is intrinsic to tuning forks. We explore the application of tapping mode to conductive AFM, where individually injected current pulses can stimulate EL when the electrostatic junction is under forward bias. This approach can be very useful for the characterization of nanostructures such as those based on carbon nanotubes, which are damaged easily under the force sustained by the tip in contact mode. We have applied this method to map the electroluminescence of *p-n* junctions in Cu(In,Ga)Se₂ solar cells, revealing local fluctuations in photon intensity and energy.

NN10.18

Nanoscale Piezoelectric and Nonlinear Dielectric Response across a Single 180° Ferroelectric Domain Wall. Lili Tian¹, Venkatraman Gopalan¹, David A. Scrymgeour², Tomoyuki Sugihara³, Koya Ohara³ and Yasuo Cho³; ¹Pennsylvania State University, University Park, Pennsylvania; ²Sandia National Laboratories, Albuquerque, New Mexico; ³Tohoku University, Sendai, Japan.

Local electromechanical response and nonlinear dielectric response across a single 180° domain wall in ferroelectric lithium tantalate crystal were investigated by using piezoelectric force microscope and scanning nonlinear dielectric microscope. The linear dielectric change, nonlinear dielectric response, and asymmetry in local electromechanical response were observed across the domain wall. Finite Element Method was used to model the response between a conductive tip and the ferroelectric surface with a single domain wall. Excellent qualitative agreement, and order of magnitude quantitative agreement is found between experiments and modeling. Surprising local features near the wall are observed, which are correlated with crystal stoichiometry. The interaction widths of the domain wall in both piezoelectric force microscopy and scanning nonlinear dielectric response will be discussed.

NN10.19

Biomolecular Adhesion Between Opposing Cartilage Aggrecan Macromolecules. Lin Han¹, Delphine Dean², Laura A. Daher¹, Alan J. Grodzinsky^{2,3,4} and Christine Ortiz^{1,4}; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Biological Engineering Division, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Aggrecan, the most abundant proteoglycan in the cartilage extracellular matrix (ECM), is a comb-like polyelectrolyte with highly negatively charged polysaccharide glycosaminoglycan (GAG) side chains (contour length, $L_{contour}$ 40 nm) covalently attached and closely spaced (2-4 nm) along a protein core backbone ($L_{contour}$ 400 nm). Our previous studies have focused mainly on repulsive interactions between opposing aggrecan upon loading (Dean et al., 2005, Ortho. Res. Soc.). In this study, high resolution force spectroscopy (HRFS) was employed to examine the interactions upon unloading after compression ("retraction") between micron-sized colloidal probe tips (R_{tip} 2.5 μ m) with 10⁴ chemically end-grafted fetal epiphyseal aggrecan and similar aggrecan-functionalized planar substrates. Dimethylmethylene blue dye assay was performed after removing aggrecan from the substrates by boiling and yielded a molecular separation distance of 20 nm. A colloidal probe tip functionalized with HS(CH₂)₁₁OH, (a hydroxyl-terminated self-assembled monolayer or OH-SAM) was used as the neutral

control. For the OH-SAM probe tip vs. aggrecan-functionalized substrate in 0.001M - 1.0M NaCl (pH = 5.6) with a maximum compressive load, P_{max} , 50 nN and displacement rate, z , = 4 $\mu\text{m/s}$, long range, nonlinear attractive forces were observed upon retraction for t (time held at maximum load) > 1 second(s). Under these experimental conditions, the maximum attractive force was found to increase with IS, varying from 0.6±0.1 nN at 0.01M and 0.001M to 3.0±0.8 nN at 1.0M at $t = 30\text{s}$ ($p < 0.0001$). The maximum distance at which the probe tip detached from the substrate (i.e. the force returned to zero) for these experimental conditions were 410±100 nm for all IS, approximately the same as the contour length of the aggrecan core protein. There was no significant dependence of maximum attractive force or detachment distance on P_{max} or z for all IS values. For aggrecan vs. aggrecan experiments, the trends in the data were similar to that observed for the neutral colloid. The maximum attractive forces were larger compared to those obtained with the neutral colloid, varying from 2.3±0.6 nN at 0.01M and 0.001M to 4.5±0.8 nN at 1.0M ($p < 0.0001$) for P_{max} 50 nN, $z = 4 \mu\text{m/s}$, $t = 30 \text{ sec}$. The maximum detachment distances for these experimental conditions were 755±145 nm for all IS, approximately $2 \times L_{contour}$ of the aggrecan core protein. Recent biochemical studies have shown that aggrecan can bind to as fibulin-II, a protein in the ECM via the carboxyl-terminal G3 domain. Ongoing studies involve the use of HRFS to quantify the type and extent of aggrecan binding interactions, for example with collagen and other biomolecules relevant to biological tissues.

NN10.20

A New Statistical Approach for the Quantitative Analysis of Single-Molecule Force Spectroscopy Data. Alexei A. Valiaev^{1,4}, Ashutosh Chilkoti^{2,4}, Stefan Zauscher^{1,4} and Scott Schmidler³, ¹Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina; ²Department of Biomedical Engineering, Duke University, Durham, North Carolina; ³Institute of Statistics and Decision Sciences, Duke University, Durham, North Carolina; ⁴Center for Biologically Inspired Materials and Materials Systems, Duke University, Durham, North Carolina.

We demonstrate a new statistical approach for the quantitative characterization and analysis of force-extension curves obtained from single-molecule force spectroscopy (SMFS) measurements. We tested our statistical methodology on force-extension data obtained from stretching elastin-like polypeptides (ELPs) that contain repeats of the five amino acids Val-Pro-Gly-Xaa-Gly (VPGXG), where Xaa is a guest residue. Since the peptide sequence and thus the molecular architecture of ELPs can be precisely controlled and easily modified using genetic engineering methods, these polypeptides are particularly well suited to demonstrate our analysis method. A critical aspect for comparing fit parameters obtained for different experimental conditions or for structural variants is to quantify the uncertainty in the estimated fit parameters. In our statistical approach, we used a nonparametric Monte Carlo bootstrapping procedure to obtain sampling distributions and confidence intervals for the fitted parameters. In the analysis of SMFS data, we first accounted for the increased variance in the measurements at lower forces (increased thermal noise) using an iteratively-reweighted least-squares procedure. Second, we introduced a model that combined data from multiple curves measured under the same experimental conditions to reduce variability in the parameter estimation. We further increased the accuracy of the model parameters estimation by simulating the noise in force and extension simultaneously using Bayesian Markov chain Monte Carlo methods. Results indicated that our new data analysis method is able to distinguish small differences in the molecular architecture of ELPs from SMFC experiments. For example, we are now able to resolve differences in Kuhn segment lengths as small as 0.01 nm, i.e., significantly smaller than those reported previously. We believe that our approach is universally applicable to SMFS data and of interest for the analysis of structure-property relations in polymers and biomacromolecules.

SESSION NN11: Scanning Probes Applied to Magnetic Materials

Chair: J.C. Seamus Davis
Thursday Morning, December 1, 2005
Back Bay C (Sheraton)

8:30 AM NN11.1

Determination of the uncompensated spin density in antiferromagnetic/ferromagnetic multilayers by MFM. Peter Kappenberger¹, Magdalena Parlinska-Wojtan¹, Iris Schmid² and Hans Josef Hug^{1,2}; ¹Laboratory for Nanoscale Materials Science, EMPA, Dübendorf, Switzerland; ²Institute of Physics, University of Basel, Basel, Switzerland.

The balance between exchange, anisotropy and dipolar energies usually determines the domain structure in ferromagnetic (FM) films.

However, coupling a ferromagnetic (FM) film to an antiferromagnetic (AF) layer can significantly alter the hysteresis processes and domain structure due to the additional FM-AF-interfacial exchange [1,2]. Exchange biasing results from field cooling such a sample through the Neel temperature (T_n) of the AF. The FM-AF interaction provides an effective bias field that gives rise to a horizontal shift in the hysteresis loop, increases the anisotropy of the FM-layer and often enhances the coercive fields. As such, exchange biasing has become an important tool for controlling domain formation in magnetic devices [3]. While routinely exploited the microscopic origin of exchange bias is still open to debate. In this contribution, we describe quantitative high-field magnetic force microscopy (MFM) measurements of the spatial distribution of uncompensated spins in perpendicularly exchange-biased CoO/(CoPt) multilayer and single layers [4]. The samples were cooled through T_n of CoO in a well-defined striped domain pattern [5]. At 8K, external fields up to 7T were applied to saturate the FM-layers and the remaining uncompensated spins could be imaged with high lateral resolution [6]. Qualitatively, we find that the uncompensated spins replicate the original ferromagnetic domain structure but are antiferromagnetically aligned to the ferromagnetic moments. Upon field reversal the original domain structure returns, showing a direct link between the uncompensated spins and the local bias. Quantitative analysis of the MFM images revealed that 7% of the AF spins at the interface are uncompensated and contribute to the exchange biasing [6]. This agrees well with existing literature values between 1% and 8% on similar systems [7,8]. Based on high resolution MFM and TEM measurements, we derived a simple model that can explain the small amount of uncompensated spins. It also accounts for the observation of wrongly aligned grains in the AF. We will also propose a possibility by which the number of uncompensated spins and hence the AF-coupling could be increased significantly. [1] A.E. Berkowitz and K.Takano, J. Magn. Magn. Mat. 200 (1999) 552. [2] J. Nogues and I.K. Schuller, J. Magn. Magn. Mat. 192 (1999) 203. [3] J.C. S. Kools, IEEE Trans. Magn. 32 (1996) 3165. [4] S. Maat, K.Takano et al., Phys. Rev. Lett. 87 (2001) 087202. [5] O. Hellwig, et al., Physica B 336 (2003) 136. [6] P. Kappenberger et al., Phys. Rev. Lett. 91 (2003) 2672021. [7] H. Ohldag et al. Phys. Rev. Lett. 91 (2003) 017203. [8] A. Scholl et al., Appl. Phys. Lett. 85 (2004) 4085.

8:45 AM *NN11.2

Imaging, Manipulation, and Spectroscopic Measurements of Nanomagnets by Magnetic Force Microscopy. Peter H. Grutter, Physics, McGill University, Montreal, Quebec, Canada.

Magnetic force microscopy is a very powerful tool with which to study magnetic nanostructures. In cooperation with external magnetic fields, MFM can be used to study the magnetization switching mechanism of submicrometer-sized magnetic particles. MFM can thus be viewed as a magnetometer with spatial resolution, allowing insights into the poorly understood magnetic reversal modes of these systems. If a better control of the switching field distribution can be obtained it might become possible to use small magnetic particles in a cellular automata architecture allowing the potential implementation of nanoscale memories or processors and thus an alternative to molecular electronics [Cowburn et al., NJP 1, 16.1 (1999)]. Various MFM techniques allow the measurement of a hysteresis curve of an individual particle, which can then be compared to ensemble measurements. The advantage of using MFM-constructed hysteresis loops is that one can in principle understand the origin of dispersion in switching fields, hence the concept of a spatially resolving magnetometer. It is also possible to directly observe the correlation between magnetic particles through careful imaging and control of the external magnetic field. In all of these measurements, attention needs to be paid to avoid artifacts that result from the unavoidable magnetic tip stray field. Control can be achieved by optimizing the MFM operation mode as well as the tip parameters. It is even possible to use the tip stray field to locally and reproducibly manipulate the magnetic moment state of small particles. In this talk, I will illustrate these concepts and issues by discussing studies of various lithographically patterned magnetic nanoparticles, thus demonstrating the versatility of MFM for imaging, manipulation, and spectroscopic measurements of small particles.

9:15 AM NN11.3

Magnetic Force Microscopy of Bulk L1o-Ordered Intermetallic FePd Ferromagnets with Equiaxed Grain Morphology. Paul R. Ohodnicki^{1,2}, Anirudha R. Deshpande¹ and Jorg M. K. Wiezorek¹; ¹MSE, University of Pittsburgh, Pittsburgh, Pennsylvania; ²MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania.

The L1o-ordered intermetallic phase FePd is a member of a class of uniaxial ferromagnetic intermetallics with very large magnetocrystalline anisotropy, also including FePt and CoPt. The technologically relevant properties of these permanent magnets depend very strongly on the microstructure (morphology and scale) and defect structure produced during processing. Order-annealing

after intense cold-deformation has been used to fabricate bulk equiatomic FePd alloys with morphologically equiaxed microstructures and average grain sizes ranging from the submicron- to the micron-scale. Alloys processed in this manner exhibit up to a six-fold enhanced coercivity relative to conventionally processed FePd and a 'Hall-Petch'-type relationship has been established between the coercivity and the average grain size in the ordered state. Developing an understanding of the magnetization reversal behavior and dominant coercivity mechanisms requires knowledge of the details of the interplay between the magnetic domain structure and relevant features of the alloy microstructure. Here, magnetic force microscopy (MFM) techniques have been used for the first time to reveal experimentally both the magnetic domain structure and the microstructure of these polycrystalline intermetallic alloys. The MFM studies uniquely facilitated the direct correlation between microstructural features (e.g. grain boundaries and other crystal defects) and the magnetic domain structure with spatial resolution on the order of 10nm. Implications of our MFM studies for the understanding of magnetic properties and behavior of these FePd-based ferromagnets are discussed. Support from the National Science Foundation (DMR-0094213) and access to the SPM facility of J.A. Barnard is gratefully acknowledged.

9:30 AM NN11.4

MFM/AFM Study of Electroplated Fe₅₀Ni₅₀ Films. Qi Zeng¹, Ian Baker¹ and Charles P. Daghljan²; ¹Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire; ²Rippel Electron Microscopy Facility, Dartmouth College, Hanover, New Hampshire.

Fe-Ni alloy thin films find uses in magnetic recording heads cores due to their low coercivity, high permeability, near zero magnetostriction, and good corrosion resistance. Fe₅₀Ni₅₀, the focus of this study, has the highest saturation magnetization amongst Fe-Ni alloys. The surface morphology, magnetic domain structure, as well as the magnetic properties of electroplated Fe₅₀Ni₅₀ films, were studied by magnetic force microscopy and atomic force microscopy. The current density during electroplating was varied from 1 - 100 mA/cm². The plated films consisted of 100 nm spherical particles. As the current density increased, the particle size did not change, but the grain size decreased from 17 to 8 nm, and strip-like magnetic domains, larger than both the grain and particle size, became less pronounced, indicating a decrease in the perpendicular magnetic component. No magnetic domains were observed in the films plated with current densities of 50 A/cm² or greater. The decrease in grain size was accompanied by an increase in the surface roughness, as the current density increased. Current density also affected the coercivity and the in-plane anisotropy of the films. As the current density increased, the coercivity increased, and the squareness of the hysteresis loops decreased. The in-plane anisotropy may arise from the in-plane texture. Research sponsored by NIST grant 60NANB2D0120.

9:45 AM NN11.5

Magnetic domain imaging using ultrafine Co particles produced by sputtering from a nanoparticle gun.

Prasanna Shah and Andrew Gavrin; Physics, Indiana Univ Purdue Univ at Indianapolis, Indianapolis 46202, Indiana.

Cobalt particles have been synthesized using high pressure sputtering in a specialized particle source developed in our laboratory. This source consists of a magnetron sputtering gun fitted with a cover plate that may incorporate a variety of aperture or nozzle geometries. Predominantly, the Co-fcc phase is produced, as evidenced by X-ray diffraction measurements. Average grain size determined by atomic force measurements in tapping mode and line broadening analysis of the main peak in X-ray diffraction is in the range 25-50 nm. We have employed these particles for magnetic domain imaging using the High Resolution Bitter Microscopy (HRBM) method described in our earlier work [1]. Similar to our results with Fe nanoparticles, we find that the Co nanoparticles are preferentially deposited along domain walls, allowing the domain structure to be imaged using optical or scanning electron microscopy. The pressure in the gun is in the range 600 - 1000 mT with the sputtering power 50 W. Efforts to improve the contrast by varying sputtering parameters and source aperture plates are underway. [1] Prasanna Shah, Andrew Gavrin, "Synthesis of nanoparticles using high pressure sputtering for magnetic domain imaging", submitted to Journal of Magnetism and Magnetic Materials.

SESSION NN12: Electronic Materials Studied with Scanning Probes I

Chairs: Raffi Budakian and Toyohiko Kinoshita
Thursday Morning, December 1, 2005
Back Bay C (Sheraton)

10:30 AM NN12.1

Kelvin Probe Force Microscopy Investigations of Single Wall

Carbon Nanotubes on SiO₂ chemically modified with Self-assembled Monolayer films. Yuji Miyato¹, Kei Kobayashi², Kazumi Matsushige^{1,2} and Hirofumi Yamada^{1,3}; ¹Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; ²International Innovation Center, Kyoto University, Kyoto, Japan; ³Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Kyoto, Japan.

Single wall carbon nanotubes (SWNTs) are promising candidates for building nano-blocks of next-generation electronic devices because of their unique electrical and mechanical properties. In particular, carbon nanotube field effect transistors (CN-FETs) using semiconducting SWNTs deposited on SiO₂ / Si substrates have been intensively studied. However, we have often observed a large drain current hysteresis reflecting the history of the applied gate bias voltages. This hysteresis might be caused by some charge accidentally injected into water layers existing on the hydrophilic SiO₂ surface. In this study, we chemically modified the SiO₂ surface to decrease the interfacial energy by covering it with a hydrophobic self-assemble monolayer (SAM) film. The surface potential mapping along the SWNTs was performed by Kelvin probe Force Microscopy (KFM), which is a powerful tool for the investigations of electronic states on a nanometer scale. The surface potential distribution of CN-FETs made on the bare SiO₂ substrate was compared to the one on the SAM modified substrate in various bias condition in order to evaluate the effect of the SAM modification on the current hysteresis. We used hexamethyldisilazane (HMDS) and octadecyltriethoxysilane for making SAM films. Both vapors react with hydroxyl groups on the SiO₂ surface and then trimethylsiloxane (TMS) and octadecylsiloxane (ODS) monolayer films are made respectively. We deposited SWNTs on the bare SiO₂ substrates and on the substrates modified with these SAM films. The SWNTs were connected to the Au source and drain electrodes by AC dielectrophoresis method. The KFM measurements showed that the hysteresis behavior in surface potential of the CN-FETs on the substrates modified with the SAM films was drastically reduced compared to the CN-FETs on the bare SiO₂. The results indicate that the charge density in the water layer on the hydrophilic substrate is changed depending on the bias condition, consequently causing the current hysteresis. The SAM films can effectively exclude the water layer and prevent charges from diffusing onto the substrate.

10:45 AM NN12.2

Scanning Tunneling Microscope Study of Interaction Among Carbon Based Quantum Structures. Gurbrinder Singh Khara and Jaewu Choi; Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

The unique physical properties of carbon-based quantum structures such as single walled carbon nanotubes and fullerenes have attracted lot of attention from scientific and technological community. Large amount of studies on these individual structures exist. However, there is not much study on the interaction between carbon based quantum structures, which could offer very unique opportunity for future single molecular scale devices. In this paper, we will present the study on the interaction between single walled carbon nanotube (SWCNT) and fullerenes on highly oriented pyrolytic graphite (HOPG) using a VT-UHV Scanning Tunneling Microscope. Scanning tunneling spectroscopic study reveals the modification of the electronic structures of individual carbon nanotube and fullerenes due to the physical interaction between them.

11:00 AM NN12.3

Correlated electrical and structural properties of GaN nanowire based devices. Goutam Koley¹, L. Lakshmanan¹, A. Khan¹, Ho-Young Cha², H. Wu² and M. G. Spencer²; ¹Electrical Engineering, University of South Carolina, Columbia, South Carolina; ²Electrical Engineering, Cornell University, Ithaca, New York.

Electrical and structural properties of GaN nanowires (20 nm typical diameter) grown by direct reaction between metallic Ga and ammonia have been studied and correlated. GaN nanowires were grown on SiO₂ covered doped Si substrates using Ni catalyst, and metal contacts (stack of Ti/Al/Mo/Au) were deposited at the two ends (nominally 4 micron apart) using a novel pre-aligned nanowire growth and fabrication process, to fabricate backgated FETs with the Si substrate as gate terminal. The I-V curves showed saturation in many cases, and single nanowire FETs have shown saturation currents as much as 3 to 4 microamperes. Interesting behavior of the nanowire devices were observed when I-V characteristics were measured in two-terminal configuration with only the source and drain bias. The devices studied could be categorized into ones showing purely schottky characteristics, purely ohmic characteristics, premature saturation, and those showing drain current dependency on the direction of the bias sweep. Since the ohmic contact metal stack was not annealed (to avoid damage to the SiO₂ insulator and shorting) the schottky contact formation is not surprising, and schottky barrier heights of 0.7 eV have preliminarily

been estimated from the I-V characteristics. The devices showing variable drain current exhibited two different states of drain current for the same bias, depending on the direction of the sweep. Structural characterization using scanning probe microscopy was performed to explain the difference in electrical characteristics observed for different devices. It was found out that devices showing schottky characteristics usually consist of a single nanowire, whereas those showing ohmic characteristics usually consist of several nanowires. The schottky contact is formed at the source side where the nanowires originally grow from the Ni catalysts. Detailed investigations are being carried out with surface potential and scanning gate measurements to characterize the metallic contacts and the nanowires, and a unified model explaining the experimental observations will be presented.

11:15 AM NN12.4

Ballistic Electron Emission Microscopy on 2D-patterned GaN_xAs_{1-x} quantum dots fabricated using ion implantation followed by pulsed laser melting. TaeSeok Kim, Michael J. Aziz and Venkatesh Narayanamurti; Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

We will present Ballistic Electron Emission Microscopy (BEEEM) measurements on 2D patterned GaN_xAs_{1-x} nanostructures fabricated in a GaAs matrix using nitrogen ion implantation followed by pulsed laser melting and rapid thermal annealing (RTA). As a three terminal scanning tunneling microscopy technique, BEEEM can image both the surface topography and the local hot electron transport. Using ion implantation through a lithographically patterned mask and varying subsequent processing conditions, we have made locally confined GaN_xAs_{1-x} dots with different activated nitrogen concentrations. By analyzing BEEEM images, we study giant bandgap bowing effects on the Schottky barrier height. We will also discuss the effects of undoped layer thicknesses, laser fluences and RTA conditions on the conduction band structures of these quantum dots.

11:30 AM NN12.5

Atomic Force Probing in 65nm MOSFETs SRAM Cells. Kim Christensen¹, Juan Rosal¹, Andy Erickson² and Roger Alvis²; ¹Silicon Technology Development, Texas Instruments, Inc, Dallas, Texas; ²Multiprobe, Inc, Santa Barbara, California.

Nano probing is accomplished with the help of an Atomic Force Probing (AFP) tool. The inherent resolution and positioning accuracy of Scanned Probe Microscopy (SPM) has allowed a wide variety of measurements to be accomplished at submicron scale. Electrical measurements by SPM are of particular interest to the semiconductor industry as circuit and device dimensions shrink to the nanoscale. This paper will discuss the application of an AFP tool for characterizing 65nm transistors in SRAM cells. SRAM characterization is the preferred method for process development within the semiconductor industry. Many of the SRAM failures are soft or intermittent type of failures and the standard techniques of physical failure analysis such as delayering and optical/SEM inspection or cross-sectional analysis by FIB/TEM is increasingly providing no visual defect results. Use of electrical probing of the individual SRAM transistors can provide new insight into the root cause of failure that can provide feedback for the process development of leading edge technologies. For the purposes of characterizing the electrical performance or failures of fully functional semiconductor devices, IV spectra are required. In order to make contact to today's leading edge devices, probes with radii on the nanometer length scale must be brought into contact with the terminals of these devices. This is simply no longer possible without the aid of a high magnification viewing. Neither the terminals nor the probe tip is visible in the highest power optical microscope and without some form of feedback, even the most skilled operator will bend the tiny probe tip or damage the invisible device. The scanned probe microscope is a solution to the issues of magnification and force control with typical Atomic Force Microscopy (AFM) values of 100kX and nanoNewton sensitivity. For the purposes of nano probing however, the single probe AFM is incomplete since there are typically 2 or more contacts required for IV measurements of devices and circuits. The probing position is determined from the AFM image created by each probe wire tip. The probes must be independently controlled to allow arbitrary positioning onto the contacts of a device but must not interfere with each other while creating the images used for positioning the probes. In the AFP instrument synchronous scanning is used to both increase the speed with which the images are acquired and to avoid collisions between probes. Scanning takes place with the probe tips spacing of about 0.5µm and probe placement required for 65nm devices is routinely within <200nm tip to tip spacing. Examples of how the electrical transistor data has provided insight into the root cause of failure for the SRAM transistors and provided feedback for the process development will be demonstrated in this paper.

11:45 AM NN12.6

Visualization of Charges Stored in Flash memories using the

Scanning Nonlinear Dielectric Microscopy. Koichiro Honda¹, Sunao Hashimoto² and Yasuo Cho²; ¹Fujitsu Ltd., Atsugi, Japan; ²RIEC, Tohoku University, Sendai, Japan.

By applying Scanning Nonlinear Dielectric Microscopy (SNDM), we have succeeded in clarifying the position where electrons/holes are located in the gate thin SiO₂-Si₃N₄-SiO₂ (ONO) film of the MONOS type flash memory. Following this, we succeeded in clarifying the electrons existed in the poly-Si layer of the floating gate (FG) of flash memory. SNDM is one of the microwave microscopy measurement techniques using an atomic force microscopy where a ring electrode is used in conjugation with a cantilever. Alternating electric field is biased between this electrode and the sample, and the capacitance variation of the surface region of the sample is detected. In the MONOS case, the charge accumulated in the ONO film can be detected by SNDM as a change in capacitance by scanning the surface of the ONO film. In the SNDM image, a bright contrast existed in the neighborhood of the source in the channel area, when electrons were injected. On the other hand, a black contrast existed in the source neighborhood in the channel area, when holes were injected. In the Floating gate type, the charge accumulated in the floating gate can be detected by SNDM as a change in capacitance the poly-Si (floating gate) by scanning the surface of the ONO film covering the floating gate. In the SNDM image, a black contrast existed in the floating gate area, where electrons were injected. On the other hand, there appeared no clear contrast of the floating gate when electrons were not injected. In the MONOS case, these images can be interpreted as a visualization of the polarization of the electron-hole pair. When the positive charge exists in the insulating film, the polarization capacity decreases (dC/dV < 0) as the electric field is impressed from the substrate side. Therefore, the contrast becomes black. On the other hand, when the minus charge exists in the ONO film, capacitance grows (dC/dV > 0), and the contrast becomes white as the electric field is impressed from the substrate side. Therefore, the SNDM signal will be reversed by the positive and negative charge in the ONO film. In the FG case, these images can be interpreted as the visualization of the change of depletion layer, when the electrons are injected in the poly-Si. When the electric field is impressed from the substrate side, carriers move to the substrate side, and the capacitance of the poly-Si becomes small. (dC/dV < 0). Then, the contrast becomes dark. Therefore, the SNDM signal contrast appeared when charge is stored in the floating gate. As shown, SNDM is a powerful method for visualizing charge spatial location in a dielectric material.

SESSION NN13: Electronic Materials Studied with Scanning Probes II
Chair: Raffi Budakian
Thursday Afternoon, December 1, 2005
Back Bay C (Sheraton)

1:30 PM NN13.1

Thermal Characterization of Joule Heated Nanostructures by Surface Potential Imaging Microscopy. Abhishek Jain, Lisa Pietruszka, Hao Ming Huang and Theodorian Borca-Tasciuc; Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Thermal characterization of nanostructures is critical for understanding thermal transport at nanoscale and for design and operation of nanoelectronics and novel thermo-electric energy conversion devices. There is a need to develop fast and reliable techniques to measure the thermal response of individual nanostructures during operation, when electric current passes through the nanodevices. Here is described the development of a method for thermal characterization of electrically conductive individual nanowires. In this method the nanowire specimens are suspended between patterned microelectrodes on an electrically insulated substrate. If the transport is diffusive the passage of direct current through the specimen causes a DC temperature change due to Joule heating along the wire. The average temperature rise of the wire is determined from the change in the electrical resistance and hence the change in the voltage drop across the nanowire. The voltage drop is monitored using the surface potential imaging mode of a scanning probe microscope. The thermal conductivity of the nanostructure is determined by fitting the measured temperature rise with predictions of a thermal model that takes into account the major heat transfer mechanisms in the system. The paper presents the calibration of the method and proof of principle demonstration of thermal conductivity measurements on carbon nanotube bundles.

1:45 PM NN13.2

Lateral Electron Transport Across Individual Grain Boundaries Investigated by Electro-Assisted Scanning Tunneling Microscopy. Manuel J. Romero, Chun-Sheng Jiang, Rommel Noufi and Mowafak M. Al-Jassim; National Renewable

Energy Laboratory, Golden, Colorado.

We report on a novel approach to investigate lateral electron transport in semiconductors based on a combination of scanning tunneling microscopy (STM) with the excitation provided by the electron beam in electron microscopy - or electro-assisted STM. In simple terms, the electron beam excites electrons and holes at specific locations in the semiconductor and their effect on the tunneling current is measured. The physics of the electro-assisted tunneling current is comparable to the photocurrent when the STM is operated under external illumination. On the other hand, electro-assisted STM can be thought of as a two-probe microscopy because electron beam and STM tip can be controlled simultaneously and independently. For the purpose of illustration, we have investigated the electron transport across individual grain boundaries in *p*-type Cu(In,Ga)Se₂(CIGS) thin films. This is performed maintaining the STM tip over one grain and measuring the difference in tunneling current when electrons are excited within that particular grain and across the grain boundary when scanning the electron beam. Using this method, we report evidence for a significant barrier for electron diffusion across grain boundaries in CuGaSe₂, which is not present in CuInSe₂. These transport measurements can be implemented in other forms of scanning probe microscopy, such as conductive atomic force microscopy (AFM). In this case, the current induced by the electron beam is measured by a conducting tip under force feedback control. Our progress in this area is also presented.

2:00 PM *NN13.3

Atomic-Resolution 'Mottness Mapping' in Lightly Hole-Doped Cuprates. J. C. Seamus Davis, Physics, Cornell University, Ithaca, New York.

I will introduce new spectroscopic STM techniques for atomic resolution imaging of the locations of holes in doped Mott insulators (such as high-T_c cuprates or CMR manganites). I will then describe application of these techniques in studies designed to determine the identity of the electronic phase intervening between the antiferromagnetic Mott insulator at zero doping and the high-T_c superconducting phase at higher hole doping. This phase is the only unidentified phase in the system and, at least as a function of dopant density, is the true parent phase of the superconductivity.

2:30 PM NN13.4

Structure and Charge Density Waves of K_{0.3}MoO₃ (blue bronze) (20-1) Surfaces by Variable Temperature STM. Maxim P. Nikiforov¹, Abdel F. Isakovic², Robert E. Thorne² and Dawn A. Bonnell¹; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Physics Department, Cornell University, Ithaca, New York.

Scanning Tunneling Microscopy (STM) has been used extensively in the study of charge density waves (CDW) in hexagonal compounds such as NbSe₂, α-TaSe₂, α-TaS₂ etc. A limited number of studies have been done of the surfaces of K_{0.3}MoO₃ (blue bronze), a monoclinic compound. To date, charge density waves on blue bronze have not been imaged by STM. In this work we demonstrate unit cell spatial resolution on the blue bronze (20-1) surface at room temperature and at 110K. The contrast in images obtained at room temperature is attributed to the surface atomic structure. At room temperature the tip state plays an important role in the contrast formation, as indicated by the observation of three different images of the (20-1) surface of K_{0.3}MoO₃. We attribute these variations to different tip end atoms: W, Mo and O. At low temperature charge density waves are superimposed on the unit cell resolution pattern. The comparison between CDW in hexagonal compounds like NbSe₂ and monoclinic compounds like K_{0.3}MoO₃ and NbSe₃ will be made. To the best of our knowledge this is the first observation of charge density waves on blue bronze by STM.

2:45 PM NN13.5

Detecting Electrostatic Surface Potentials by Multimode Electrostatic Force Microscopy in Ambient. Nicola Naujoks¹, Robert W Stark² and Andreas Stemmer¹; ¹Nanotechnology Group, Swiss Federal Institute of Technology, Zurich, Switzerland; ²Ludwig-Maximilians-Universitaet, Munchen, Germany.

For the development of novel nanoelectronic devices, the ability to inject and detect charges with nanometer spatial resolution is a fundamental prerequisite. Based on the high resolution capability of atomic force microscopy (AFM), several methods of electrostatic force microscopy (EFM) evolved for the detection of charge patterns and local contact potential differences. In ambient conditions, Kelvin probe force microscopy (KPFM)^{1,2} is applied to measure the surface potential in a two pass technique. After imaging the specimen in conventional tapping mode AFM, the surface potential is determined by KFM in a second pass, lifted a few nm above the surface. A simultaneous measurement of topography and contact potential

difference is achieved by multifrequency EFM methods that have been introduced for operation under ultra-high vacuum conditions^{3,4}. The electrostatic interaction is detected at a frequency different from the mechanical driving frequency of the cantilever. While the fundamental mode is used for distance regulation during non-contact imaging, the second eigenmode of the cantilever is used to detect the electrostatic signal. When using amplitude modulation for distance regulation, like it is done in ambient conditions, it is known that non-linear dynamics give rise to higher harmonics of the mechanical driving frequency⁵. Thus, in order to apply the single pass approach of multimode (MM) EFM for the detection of electrostatic potentials in ambient, the question of spectral interference between topographic imaging and MM-EFM has to be answered. MM-EFM was investigated by detecting electrical charges on PMMA, and comparing these results to measurements obtained with KFM. The charges have been injected into the PMMA substrate following a standard procedure⁶. While imaging the topography at the fundamental frequency at 51.0 kHz, the third flexural mode at 693.4 kHz was used for detection of the electrostatic forces by MM-EFM. The power spectrum of the multimodal EFM signal shows the 3rd eigenmode to be well separated from mechanically induced higher harmonics due to mechanical tip sample interaction. As these higher harmonics are located around the 2nd eigenmode, and their signals are in the same order of magnitude, this mode does not seem to be favorable for MM EFM under ambient conditions. MM-EFM images show that injected charges can be detected at spatial resolution comparable to KFM. The topography is well reproduced in multimode EFM without additional noise. 1 M. Nonnenmacher, M. P. O'Boyle, H. K. Wickramasinghe, Appl. Phys. Lett. 58, 2921, 1991. 2 H. O. Jacobs, H. F. Knapp, A. Stemmer, Rev. Sci. Instrum. 70, 1756 (1999). 3 A. Kikukawa, S. Hosaka, R. Imura, Rev. Sci. Instrum. 67, 1463 (1996). 4 Th. Glatzel, S. Sadewasser, M. Ch. Lux-Steiner, Appl. Surf. Sci. 210, 84 (2003). 5 R. W. Stark, G. Schitter, M. Stark, R. Guckenberger, A. Stemmer, Phys. Rev. B 69, 085412 (2004). 6 N. Naujoks, A. Stemmer, Microel. Eng. 78-79, 331 (2005).

3:30 PM NN13.6

Quantitative Modeling of Electrostatic Force Microscopy. Yongxing Shen¹, David M. Barnett^{1,2} and Peter M. Pinsky²;

¹Materials Science and Engineering, Stanford University, Stanford, California; ²Mechanical Engineering, Stanford University, Stanford, California.

Electrostatic force microscopy (EFM), which measures the long-range electrostatic interaction between a sample and a conductive tip of an atomic force microscope (AFM), has been applied in studies of electronic devices, ferroelectric materials and oxide bicrystals. For better interpretation of such experiments, an analytic approach has been developed to solve for the electrostatic tip-sample interaction. Unlike previous models, which either describe the tip as a simple geometric object (for instance, a sphere, a hyperboloid, a cone, a cone with a spherical apex, or a combination of these objects) or use a fictitious simple charge distribution to attempt to render the tip and sample as equipotential surfaces, our method adopts a rigorous Green's Function approach to effect a solution for realistic geometries. In our model, in order to solve the governing Laplace's equation, we are able to treat a finite computational domain with the original boundary value problem replaced by an integral equation for the unknown tip charge density. This representation permits the establishment of a variational principal for the tip-sample capacitance. The use of trial functions for the surface charge density in the variational principal yield the tip-sample capacitance accurately and efficiently. Using the associated Maxwell stress tensor, we can then easily compute the capacitive force between the tip and sample directly. To verify our results, we analyze the governing boundary value problem using the finite element method combined with an exact Dirichlet-to-Neumann (DtN) boundary condition in order to simulate the infinite domain. The two calculations agree well when the tip is relatively far away from the sample. A comparison has also been made between the present model and some previous models presented in the literature.

3:45 PM NN13.7

Study of the Processing of CdTe/CdS Solar Cells Using Conductive Atomic Force Microscopy. Helio Moutinho, Ramesh Dhare, Chun-Sheng Jiang and Mowafak Al-Jassim; National Renewable Energy Laboratory, Golden, Colorado.

Conductive atomic force microscopy (C-AFM) probes the current through a sample using the AFM tip, providing current images with high spatial resolution, as well as current versus voltage curves at well-defined spots. By providing current and topographic images from the same area, C-AFM allows for the direct correlation between electric and topographic features. We have used C-AFM to study the electrical properties of CdTe/CdS solar cells, before and after the standard treatment in CdCl₂ vapor, and after nitric/phosphoric and bromine/methanol etches used as a pre-contact treatment. We found

that the current, in most cases, was dominated by a rectifying junction between the tip and the sample surface, and the current images were very sensitive to changes in the property of the material in this region. The as-deposited samples had grains with different conductivities, and there were no significant grain-boundary effects. The CdCl₂ treatment resulted in an increase in the current, possibly due to an increase in the conductivity of the CdTe film. The bromine/methanol etch resulted in more-conductive grain boundaries as compared to intragrain material, whereas the nitric/phosphoric etch increased the conductivity of the whole film close to the surface, which is advantageous for producing high-quality devices. We did not notice any effect of illumination on the current images, except for the devices etched with the nitric/phosphoric solution, which showed a strong photogenerated current. Finally, we analyzed the cross section of etched samples. The nitric/phosphoric etch penetrated more deeply than the bromine/methanol etch, and penetration was enhanced at grain boundaries for both treatments. Based on these results, we discuss the effects of both etch treatments on the electrical properties of CdTe/CdS solar cells.

4:00 PM NN13.8

Material and Doping Contrast at Nanoscale Resolution Using Scattering-Type Scanning Near-Field Optical Microscopy.

Jesper Wittborn¹, Dimitri Kazantsev² and Rainer Hillenbrand²;

¹Physical Failure Analysis, Infineon Technologies AG, Munich, Germany; ²Nano-Photonics Group, Max-Planck-Institut für Biochemie, Martinsried, Germany.

The ongoing shrinking of microelectronic devices requires improved methods to achieve material and doping contrast imaging with sufficient resolution for process control, failure analysis and development. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning probe microscopy (SPM) provide nanoscale spatial resolution, but lack chemical sensitivity, as well as the ability of simultaneous mapping of material and doping contrast. Infrared spectroscopy in contrast, offers the required chemical sensitivity but its spatial resolution is limited to the micrometer scale due to diffraction. Here we demonstrate that scattering-type near-field optical microscopy (s-SNOM) operating at mid infrared wavelengths $\lambda \approx 10 \mu\text{m}$ [1, 2] can be applied for nanoscale resolved mapping of material and doping in microelectronic circuits. In our set-up back-scattered light is detected interferometrically to record both amplitude and phase. The optical near-field scattering, depending on refractive index and absorption of the sample, can be enhanced by phonon polaritons in polar dielectrics or plasmon polaritons in metals and doped semiconductors. Using a wavelength near the polariton resonance of the material of interest thus causes sharp contrast between this and other materials. Amplitude images of transistors in devices show sharp contrast between silicon, silicon oxide and metallic parts such as tungsten contacts, Ti/TiN liners, and TiSi layers, as well as between differently doped Si areas. Simultaneously recorded phase images of the same structures show clear contrast between TiSi and Ti/TiN, as well as between un-doped and doped silicon oxide layers. Silicon nitride layers as thin as 10 nm could be clearly seen in the phase images. Interestingly, they also show good contrast between Si areas of different doping concentration. The potential of s-SNOM to combine the chemical sensitivity of infrared analysis with the spatial resolution of SPM makes it a promising tool not only for analysis of microelectronic circuits but also for local analysis in almost every area of materials research. 1. R. Hillenbrand, T. Taubner, F. Keilmann, Nature 418, 159-162 (2002) 2. N. Ocelic, R. Hillenbrand, Nature Mater. 3, 606-609 (2004)

4:15 PM NN13.9

Directly Correlating Morphology with Current Generation using Near-Field Scanning Photocurrent Microscopy.

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Near-field Scanning Photocurrent Microscopy (NSPM) is a powerful new technique that allows for two-dimensional mapping of current in fully fabricated organic solar cells [1]. By rastering the light output from a near-field scanning optical microscope tip through a semi-transparent electrode across the solar cell surface it is possible to simultaneously collect height and photocurrent images with a lateral resolution that is governed by the NSOM aperture. In this paper we present NSPM measurements probing the relationship between morphology and current generation in photovoltaic devices based on p-xylene processed poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylene-diamine) [PFB] and poly(9,9'-dioctylfluorene-co-benzo-thiadiazole) [F8BT] blend films. The NSPM measurements show that current is generated within the bulk and not at the boundaries of the micron-sized phase-segregated features, with the PFB-rich regions producing four times as much current than the F8BT-rich regions for illumination through a semitransparent cathode. Photocurrent action spectra data for

illumination through the ITO indicate that the F8BT-rich regions may contribute to current when illuminated through the ITO electrode, but the lack of efficient p-type carrier collection networks, due to insufficient PFB in this phase, prevents efficient harvesting of photogenerated charges when illuminated through the cathode. The results are explained by nano-scale intermixing within the micron-sized domains, with differing extents of intermixing in the PFB- and F8BT-rich domains. References 1. McNeill, C.R.; Frohne, H.; Holdsworth, J.L.; Furst, J.E.; King, B.V.; Dastoor, P.C., Nano Letters 2004, 4, 219-223.

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Near-Field Scanning Optical Microscopy Study of Thin-Film Polycrystalline Photovoltaic Devices.

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A near-field scanning optical microscope (NSOM) has been built to optically and electrically characterize polycrystalline thin film photovoltaic devices. The NSOM is presently being used in air and at room temperature to perform spatially and spectrally resolved photocurrent and photoluminescence measurements on both planar and cross-sectional CdTe and CIGS samples. The NSOM optics allow multiple excitation wavelengths ranging from 457 nm to 950 nm to probe the device simultaneously for photocurrent measurements and also allow the capability of using different excitation sources for the photoluminescence measurements. Results on planar samples show a contrast in photocurrent between the grains and grain boundaries in certain samples. Cross-sectional measurements showing changes in photocurrent magnitude across the junctions of the CdTe devices have also been observed. The relative amplitudes of the CdTe peak (1.45 eV) and the red band of CdS (1.65 eV) were mapped using NSOM for photoluminescence measurements on planar CdS/CdTe devices. Photoluminescence intensity decreased in the presence of applied bias. Cross-sectional photoluminescence measurements showed inhomogeneity in the photoluminescence intensity along and perpendicular to the junction. The authors gratefully acknowledge support from the National Science Foundation under Grant No. DMR-0103945 and samples provided by University of Toledo and the National Renewable Energy Laboratory.