SYMPOSIUM R

Fundamentals of Nanoindentation and Nanotribology III

November 29 - December 3, 2004

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* Invited paper

SESSION R1: Nanoindentation and Nanomechanics
Chairs: Andrew Bushby and Anthony Fischer-Cripps
Monday Morning, November 29, 2004
Room 202 (Hynes)

8:30 AM R1.1
Kinking Nonlinear Elastic Solids and Spherical Nano-indentations. Michel W. Barsoum, Anand Murugaiah, Tiejun Zhen, Sandip Basu and Surya Kalidindi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

By repeatedly loading the same location, up to the same stress, with a spherical nano- indenter and the conversion of the load/depth-of-penetration curves to stress-strain curves can unambiguously show, as a result of the hardening observed between the first and subsequent indentations, that the deformations have to be dislocation-based. By combining these results with scanning electron microscopy, SEM, we conclusively show that seemingly unrelated layered solids such as graphite, hexagonal BN, ice, and mica (and thus much of geology), the layered ternary carbide and nitrides, viz. the Mn+1AXn phases, where n = 1 to 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element and X is C and/or N, can all be classified as kinking nonlinear elastic solids (KNEs). We show how our results can be explained by invoking the formation of incipient kink bands, IKBs, that give way to mobile dislocation walls, MDW, that, in turn, coalesce into kink boundaries, KBs, with increasing stress. The IKBs are fully reversible; the MDW result in plastic deformation, and the KBs explain the hardening. Since the dislocations are confined to the basal planes, they cannot entangle and can thus move reversibly over relatively large distances resulting in the dissipation of substantial amounts of energy, Wd, during each cycle. Simple compression experiments on polycrystalline cylinders yielded qualitatively similar results and the agreement between the nanoindentation and compression experiments is excellent. The ramifications of these results are far-reaching. First, they elucidate for the first time why graphite responds the way it does to stress; a 50 + year old problem. Second, we show that the hystertic mesocsopic units, HMUs, invoked to explain the behavior of nonlinear mesoscopic elastic (NME) solids, that to date had remained a mystery, are nothing but IKBs. We further claim that solids with high c/a ratios, which per force are plastically anisotropic, will deform by kinking. These kinking nonlinear elastic (KNE) solids, include layered silicates and minerals such as mica, the MAX phases, layered oxides, graphite and most probably ice. Given the diversity and ubiquity of these materials it is clear that IKBs and KBs play a much more important role in our daily life than has hitherto been appreciated. Lastly, that nanoindentations can tell us anything about how an earthquake will shake the earth, a 15 orders of magnitude span of length scales, is truly remarkable.

8:45 AM R1.2
Mechanical Properties and Indentation Size Effect of Intermetallics in Pb-free Soldering. Richard R. Chromik, Dong-Ning Wang, Richard P. Vinci and Michael R. Notis; Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

Intermetallic compounds forming at a solder/metallization interface are essential for a good metallurgical bond. However, excessive intermetallic formation typically results in decreased strength and lifetime of solder joints. Based on microhardness data in the literature and failure analysis of solder joints, decreased reliability has often been attributed to "brittle" intermetallics. This traditional understanding of the role of intermetallics in solder joints, based on macroscopic data, has neglected a more complete understanding of the mechanical behavior of these materials as a function of length scale and stress level. We have used nanoindentation to characterize the mechanical properties of various M-Sn intermetallics (M= Cu, Ag, Au)[1,2]. In most cases, these phases have been tested in diffusion couples with length scales similar to real solder joints. Many of the "brittle" intermetallics, such as Cu_6Sn_5, exhibit plasticity without fracture for the low loads of nanoindentation testing. A discussion of the mechanical properties will be presented, with special attention given to deformation behavior as a function of scale and indentation size effects observed for the Cu_6Sn_5 and AuSn intermetallics. 1. R.R. Chromik, R.P. Vinci, S.L. Allen and M.R. Notis, "Nanoindentation measurements on Cu-Sn and Ag-Sn intermetallics formed in Pb-free solder joints.", Journal of Materials Research 18, 2251 (2003). 2. R.R. Chromik, D.-N. Wang, R.P. Vinci and M.R. Notis, "Mechanical properties of Au-Sn intermetallics.", in preparation.

9:00 AM R1.3
Measurement of Crystal Lattice Rotations Under Nanoindents in Copper. Kirsten K. McLaughlin, N. A. Stelmashenko, S. J. Lloyd and W. J. Clegg; Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

The indentation size effect has been associated with geometrically necessary dislocations, which are required to obtain strain gradients in the material around the indentation. These gradients would give rise to lattice rotations; the existence of lattice rotations has been confirmed by measurements elsewhere [1]. However, progress has been limited by difficulties in making quantitative measurements of these rotations, particularly over small volumes. This work will present a technique to create a 3-D map of crystal lattice rotations throughout the plastically deformed region around a nanoindent. 1mN to 25mN nanoindents in the [001] face of single crystal copper are cross-sectioned with a focussed ion beam miller for analysis in the TEM. Sections are milled with positional accuracy similar to the foil thickness. The magnitude and axis of lattice rotation is measured by taking a sequence of convergent beam electron diffraction (CBED) patterns over the deformed region. Kikuchi lines in the CBED patterns are then fitted to simulated patterns to quantify the degree and axis of rotation. Cross-sections from several indents of the same size and orientation can be taken to create a 3-D map of the lattice rotations. Measurements have given results comparable with those obtained with plan-view TEM. The CBED technique has found rotations around the <012> axis in the plastic zone away from the indenter-metal interface, which is confirmed by the recently reported synchrotron-source X-ray microbeam analysis [1] of indents in copper. This work enables the density of geometrically necessary dislocations to be estimated everywhere in the cross-section and measured dislocation densities will be compared with estimates. This technique also allows quantitative comparison of the size and form of plastic deformation from different nanoindentation loads. [1] W. Yang et al. J. Mater. Res., 2004, 19(1), 66-72.

9:15 AM R1.4
An Experimental Evaluation of the Constant β Relating the Contact Stiffness to the Contact Area in Nanoindentation. Jeremy Harper Strader[1], Warren C. Oliver[2] and George M. Pharr[1,3]; [1]Materials Science & Engineering, University of Tennessee, Knoxville, Tennessee; [2]Nano Instruments Innovation Center, MTS Systems Corp, Oak Ridge, Tennessee; [3]Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Measurements of mechanical properties by nanoindentation with triangular pyramidal indenters like the Berkovich rely heavily upon the relationship between the contact stiffness, S, the contact area, A, and the reduced elastic modulus, E_r. This relationship is often written in the form: $S = 2\beta E_r (A/\pi)^{1/2}$, where β is a constant that depends on the geometry of the indenter. Although the most common values for β used in experimental measurements are 1 and 1.034, various theoretical analyses have yielded values as small as 1 or as large as 1.2, depending on the assumptions made to model the deformation. Here, we explore the most appropriate value of β by performing careful experiments in fused quartz with thin gold coatings applied to the surface to reveal the actual contact area when observed in the scanning electron microscope. Experiments were performed not only with the Berkovich indenter, but with five other three-sided pyramidal indenters with centerline-to-face angles ranging from 35.35^o (cube corner) to 85^o. Results are discussed as they apply to determining indenter area functions and obtaining accurate measurements of mechanical properties. * Research sponsored by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, and the SHaRE User Center at Oak Ridge National Laboratory, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:30 AM *R1.5
Pop-in Revisited: A New Approach to the Analysis of Nanoindentation Pop-in Data. George M. Pharr[1,2], Hongbin Bei[1,2], Easo P. George[1,2] and Jennifer L. Hay[3]; [1]Dept of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; [2]Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Nanoinstruments Innovation Center, MTS Systems Corp, Oak Ridge, Tennessee.

Nanoindentation pop-in events, in which the indenter suddenly and discontinuously thrusts forward into the material during the loading, are often caused by the nucleation of dislocations in otherwise dislocation free material when the theoretical shear strength is exceeded. Pop-in events are observed not only for spherical indenters, but also for sharp pyramidal indenters like the Berkovich. Analysis of pop-in data can be used to determine the theoretical strength, but to do so requires assumptions about the geometry of the indenter near its tip. To date, most analyses have been based on the assumption the tip is spherical, for which Hertzian contact mechanics can be used to determine the theoretical strength from measurements of the pop-in load. Although a good first approximation, the geometry of most Berkovich indenter tips is much more complex than this. Here, a new method of analysis is presented that uses the experimentally measured area function of the indenter to describe the tip geometry. It is shown that the tip shape can be accurately described by a simple functional form that is well-suited to closed-form elastic contact mechanics

analyses. The analyses accurately predict the load-displacement curve up to the point of pop-in, and in conjunction with elastic finite element calculations, the theoretical strength can also be determined. The method is illustrated by analyzing pop-in data from single crystals of Cr_3Si. The predicted theoretical strengths are within 10% of $G/2\pi$, where G is the shear modulus, but may be as much as 40% different than those derived by spherical (Hertzian) analysis of the same data. * Research sponsored by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, and the SHaRE Collaborative Research Center at Oak Ridge National Laboratory, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

10:30 AM *R1.6
The Mechanics of Nanoimprint Forming. Graham L. Cross, Barry S. O'Connell and John B. Pethica; Physics, SFI Trinity Nanoscience, Dublin, Ireland.

Nanoimprint and a number of other related techniques are a collection of surface patterning technologies that involve direct contact of a master template with the target surface. As such, they are governed by the laws of contacting bodies, and the mechanics involved can readily be investigated by existing indentation methods or close variants thereof. Among the many demonstrated applications of nanoimprint, lithographic resist processing has generated considerable interest due to its combination of high resolution with rapid throughput over wide areas. Pattern transfer can be achieved by the application of heat and pressure to the stamp (hot embossing), or solely by the generation of shear stress at the contact (cold forming.) In both cases we have found that elastic and viscoplastic strains are present during the forming process, the former of which can considerably alter the characteristics of the pattern transfer. The use of depth sensing instrumented indentation in conjunction with specially designed stamps and a variety of microscopy techniques has allowed us to isolate, control, and measure many of the stresses and strains directly during the imprint process. Further, in a more standard role, the indenter can be used to characterize the mechanical properties of imprinted structures. In this paper we summarize our experimental findings and conclusions on the role of important factors influencing the fidelity of the imprint process including elastic stresses, plastic deformation mechanisms, complexities in the confined deformation rheology, and choices in the form of applied stress. These are illustrated by a series of idealized experiments ranging from the squeeze flow of prepared coupons to the flat punch indentation of thin films and back extrusion into isolated cavities. A connection between these more localized experiments and the established findings and requirements of applications such as wide area lithography and functional polymer patterning will be made.

11:00 AM R1.7
The Stress Field around an Elastoplastic Indentation,.
Gang Feng[1], S. Qu[2], Y. Huang[2] and William D. Nix[1]; [1]Materials Science and Engineering, Stanford University, Stanford, California; [2]Depart of Mechanical and Industrial Engineering, University of Illinois, Urbana, Illinois.

It is important to know the stress field around an elastoplastic indentation; such knowledge is useful in predicting indentation-initiated fracture and in understanding the dislocation arrangements near the boundary of the plastic zone. This has become a classical problem in contact mechanics. A solution to this problem was developed by K.L Johnson [1]; he likened the indentation to the expansion of an internal spherical cavity in an elastic-plastic solid. The Johnson model is spherically symmetric and thus does not account for the presence of the free surface in the indentation problem. Chiang et al. [2] later modified the Johnson model to account for the effects of free surface by removing tractions created in the expanding cavity model. Yoffe [3] developed an alternative approach to account for the effects of free surface. The treatment of Chiang et al. involves a numerical method requiring intensive computation, while the Yoffe model includes an unknown material parameter B. Starting with the Johnson model and the Yoffe approach, and making use of the method provided by Chiang et al., we show that the material parameter B used by Yoffe can be calculated analytically. This leads to simple analytical expressions for the elastic field around an elastoplastic indentation. The new analytical model matches a Finite Element Analysis of this problem very well, and it also compares well with an experimentally determined stress field. Pile-up around an indentation may relax the stress, and its effect is also discussed. The new model is used to analyze the dislocation arrangements around nanoindentations on MgO. [1] K.L. Johnson, Contact Mechanics 1987, Cambridge University Press, 174. [2] S.S. Chiang, D.B. Marshall, A.G. Evans, J. Appl. Phys., 1982, 53, 298 - 311. [3] E.H. Yoffe, Phil. Mag. A., 1982, 46, 617 ? 628.

11:15 AM R1.8
Spherical Nanoindentations in Rutile, Sapphire Graphite and Mica Single Crystals. Sandip Basu, Anand Murugaiah, Michel W. Barsoum, Zheng Ming Sun, Surya R. Kalidindi and Yuri Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

The majority of nanoindentation work to date has been carried out with Berkovich indenters. In this work we show the significant advantages of repeatedly loading a spherical indenter - into the same location - into rutile, sapphire, graphite and mica single crystal surfaces. This approach allowed us to calculate the stress-strain curves, from which we obtain elastic moduli and yield points. More importantly we show that while the micromechanisms of what is occurring during the first cycle can be ambiguous (dislocation motion, microcracking, phase transformation, etc.) the shape and response of the second, and subsequent cycles, are key to unambiguously proving - in our case - that the deformations occurring are all dislocation-based. The response of the solids examined herein were similar in that the first indentations were characterized by some - and sometimes considerable - plastic deformation, followed by fully reversible, closed hysteric loops that were invariably harder than the first loops. The energies dissipated per cycle, Wd, were compared to values obtained from simple compression experiments establishing a bridge between macro- and stress-strain curves derived from nanoindentations. The agreement is excellent over 6 orders of magnitude of Wd's. In this paper we compare and contrast the stress-strain curves of mica and graphite - shown to be members of a larger class of solids, viz. of kinking nonlinear elastic or KNE solids1 - to those of rutile and sapphire. The response of KNE's is attributed to the formation of incipient2 and regular kink bands. The response of sapphire and rutile, on the other hand, is most probably due to the formation of dislocation arrays or pileups. Consistent with the reversible nature of the deformations, in most cases and despite substantial stresses under the indenter, no trace of the indentations could be found in a scanning electron microscope. 1. M. W. Barsoum, A. Murugaiah, S. R. Kalidindi and T. Zhen, Phys. Rev. Letts., in press. 2. M. W. Barsoum, T. Zhen, S. Kalidindi, M. Radovic and A. Murugaiah, Nature Materials, 2, 107-111 (2003).

11:30 AM R1.9
In Situ TEM Studies of Deformation Mechanisms During Nanoindentation in Ultrafine and Nanocrystalline Metals.
Miao Jin[1,3], Andrew M. Minor[2], Eric A. Stach[2,3] and J. W. Morris[1,3]; [1]Materials Science and Engineering, University of California, Berkeley, Berkeley, California; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Metals Program, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The mechanical properties and plastic deformation mechanisms of materials with grain sizes in the nanoscale regime (1-500 nm) are still largely debated. Many computational simulations have proposed that grain boundary sliding and/or grain rotation can become dominant deformation modes when grain sizes shrink to below some critical size (on the order of 10 nm). To date, no firm experimental confirmation of these mechanisms exists. In this work, we utilize a unique in situ nanoindentation stage for a TEM in order to gain insight into the relevant deformation mechanisms for ultrafine-grained and nanocrystalline Al films. We will present real-time videos that show that stress-induced grain growth - resulting from grain boundary migration, grain rotation and grain coalescence - is a common occurrence in these materials as the indentation proceeds. Our results suggest that grain growth and coalescence appear to be important modes of response in the deformation of ultrafine-and nanograined materials.

11:45 AM R1.10
Fundamental Investigations of Deformation and Plasticity by Combining Nanoindentation and 3D X-ray Structural Microscopy. Wenge Yang[1], B.C. Larson[1], J.Z. Tischler[1], C. Rouleau[1], Wenjun Liu[2] and G.E. Ice[1]; [1]Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]UNICAT-UIUC, Argonne, Illinois.

The x-ray structural microscopy facility developed on the UNICAT-II beamline at the Advanced Photon Source (APS) provides non-destructive measurements of local lattice rotations and residual elastic strains with submicron spatial resolution on mesoscopic length scales (tenths to hundreds of microns). By combining indentation and 3D x-ray microscopy, we have made x-ray microbeam measurements of the deformation microstructure under indents in single crystal Cu, from which micron resolution, 3D distributions of lattice rotations and geometrically necessary dislocation tensors have been obtained. In addition, we have recently incorporated a nanoindentation capability into our x-ray microscope to perform in-situ as well as ex-situ investigations of the structure and evolution of plastic and elastic deformation in ductile and brittle materials. Results of ex-situ spherical-indent deformation measurements will be presented in the

form of local lattice curvature measurements and geometrically necessary dislocation tensors and densities for Cu, and preliminary results for in situ indentation induced deformation in Si and Al will be presented. Research supported by the DOE Office of Science, Division of Materials Sciences under contract with ORNL, managed by UT-Battelle, LLC; UNI-CAT is supported by UIUC, ORNL, NIST and UOP Res., Inc; the APS is supported by the DOE.

SESSION R2/Y2: Joint Session: Nanomechanics and Tribology of Biological Materials
Chairs: David Bahr and George Pharr
Monday Afternoon, November 29, 2004
Room 202 (Hynes)

1:30 PM *R2.1/Y2.1
Coaxial Single Molecule Fluorescence and Scanning Probe Microscopies: Applications to the Study of Soft Materials.
Christopher M. Yip, Chemical Engineering / IBBME, University of Toronto, Toronto, Ontario, Canada.

We recently developed an integrated imaging platform that combines single molecule evanescent wave fluorescence imaging (and spectroscopy) with in situ scanning probe microscopy. The advantages, challenges, and potential represented by this coupled tool will be described in the context of the structure-function characteristics of nanostructured biomaterials and thin lipid films.

2:00 PM R2.2/Y2.2
Nanomechanical and Microstructural Features of Silk Films.
Donna M. Ebenstein[1], Jaehyung Park[2], David L. Kaplan[3] and Kathryn J. Wahl[1]; [1]Code 6176, U.S. Naval Research Laboratory, Washington, District of Columbia; [2]Chemical Engineering, Tufts University, Medford, Massachusetts; [3]Biomedical Engineering, Tufts University, Medford, Massachusetts.

The high strength and elasticity of silk fibers has many researchers trying to create synthetic fibers or coatings from silk proteins that have comparable mechanical properties to the native fibers of silkworms or spiders. Research has shown that silk fibroin protein can have two distinct microstructures: a less structurally organized silk I phase and a silk II phase made up of more highly structured beta-sheets. When silk fibers are spun by silkworms or spiders, the silk has a large percentage of the silk II structure, which is thought to impart much of its high strength. In this study, nanoindentation was used to investigate the mechanical properties and microstructure of silk films made from silkworm fibroin protein under a variety of different processing techniques. 12 different specimens were tested: 5 samples which underwent combinations of methanol, water, and stretching treatments; a control specimen that underwent none of those 3 treatments; and the same 6 samples following an enzymatic etching treatment. The methanol, water, and stretching treatments were investigated as techniques to increase the silk II component of the films, and hence improve their mechanical properties. The etching was expected to selectively digest the less organized silk I protein conformation, to reveal silk II structures. Two different nanoindentation techniques were used to study these films: (1) traditional quasi-static indentation, and (2) dynamic stiffness imaging. The quasi-static nanoindentation data showed that the silk films (before etching) ranged in modulus from 6.5 to 9.5 GPa, with the control specimen having a modulus of 7.6 GPa. Methanol and water treatment both resulted in increased moduli relative to the control film (> 9 GPa). Stretching alone had no measurable effect on the mechanical properties relative to the control film, but combining stretching and methanol treatment produced the sample with the lowest modulus of this group (6.5 GPa). Etching had a variable effect on the mechanical properties of the films, with the methanol-treated films showing the least change in modulus. Dynamic stiffness imaging provided information on the microstructure of the different silk films. For example, the dynamic stiffness images revealed an alignment of microstructure in the direction of strain for all the stretched specimens. In addition, dynamic stiffness revealed changes in structure after etching in many of the films. In this paper we will show how different processing treatments during silk film production can change the microstructure and mechanical properties of the resultant films.

2:15 PM R2.3/Y2.3
Nanoscale Characterization of Physisorbed Biofilms.
Michelle Emma Dickinson and Adrian B. Mann; Ceramics and Materials Engineering, Rutgers The State University Of New Jersey, Piscataway, New Jersey.

The properties and function of physisorbed proteinaceous biofilms are a major economic, ecological and biomedical issue. They are important in applications as diverse as osteointegration of biomaterials and biocorrosion of ship hulls. In this study nanoindentation and AFM have been used *invitro* to examine the acquired salivary pellicle formed *invivo* on dental enamel. This is an organic biofilm formed by the physisorption of proteins and carbohydrates on to the surface of dental enamel exposed to the oral environment. The pellicle has several key roles in oral physiology including lubrication and reduction of friction between teeth during mastication, as well as chemical protection of the enamel against acidic solutions. The mechanical properties, growth, structure and morphology of pellicle grown on clean natural and artificial ceramic surfaces has been studied. It was found that complete coverage of the enamel surface occured within the first few minutes of exposure, with the maximum thickness of 200-500nm achieved within 2 hours. The morphology of the pellicle surface was found to be a dense arrangement of globular shapes covering the whole surface of the tooth. Furthermore we have examined the effects of dietary agents such as tannins on the pellicle's properties. Tannins are phenolic compounds found commonly in food and beverages. They have a strong interaction with proteins causing a dark staining of the pellicle layer which then creates a stained effect on the teeth. The mechanical properties of pellicles after tannin treatment show a sizeable difference as revealed by changes in the nanoindentation force displacement curves. Using nanoscale dynamic mechanical analysis (nanoDMA) the viscoelastic properties of the pellicle have been studied. This has confirmed that there are substantial variations in the storage and loss modulus of pellicle with increasing exposure to tannin containing solutions. These changes in viscoelasticity impinge directly on the pellicle's performance as a lubricant and also the ease with which it can be removed using an abrasive dentrifice (toothpaste).

2:30 PM R2.4/Y2.4
Natural Contact Processes Emulated by Nanoindentation.
Susan Enders, Nato Barbakadse, Stanislav N. Gorb and Eduard Arzt; Max-Planck-Institute for Metals Research, Stuttgart, Germany.

Natural anti-adhesive surfaces are of great interest since they may serve as a model for artificial surfaces or surface treatments. Surfaces with anti-adhesive properties are, for example, one mechanism carnivorous plants use to catch their pray. In addition to diverse surface structures, layers of wax crystalloids prevent proper attachment of the insect's feet and thus their escape from the deadly trap. There are several hypotheses about the anti-attachment function of the waxy coatings. It may be due either to their chemical or wetting properties or their mechanical stability or instability, respectively. Weak crystalloids will break during contact whereas a surface with stable crystalloids results in a rough surface and may cause a decrease of the contact area between the plant surface and insect pads. With the help of selective local deformation tests performed using instrumented nanoindentation we simulated the contact formation of an insect foot and thus determined the mechanical stability of crystalloids. During the tests the contact stiffness as well as the force and displacement were recorded and from this data an estimation on the stability of the wax crystalloids was drawn. The results obtained were then compared with insects of different weight and attachment pad size.

2:45 PM R2.5/Y2.5
Nanomechanical Testing of Hydrated Biomaterials: Sample Preparation, Data Validation and Analysis.
Catherine Klapperich[2] and Jessica Kaufman[1]; [1]Department of Biomedical Engineering, Boston University, Boston, Massachusetts; [2]Department of Manufacturing Engineering, Boston University, Boston, Massachusetts.

Implants, tissue engineering scaffold materials, drug delivery and bio-micro electromechanical systems (BioMEMs) all use polymer or hydrogel materials. These applications require both mechanical performance and successful integration of the material into a biological environment. Mechanical strength, storage and loss moduli, wear resistance, surface adhesion properties and surface chemical composition are all critical in biomedical device design and can be determined using nanoindentation. The difficulty of obtaining large samples of specialized materials and the complexity of testing soft materials in traditional materials testing apparatus, make nanoindentation an attractive alternative. Our previous research using nanoindentation to measure the surface mechanical properties of non-hydrated polymers led to improvement in nanoindentation testing protocols. One of the major challenges in using this technique for soft materials is maintaining and controlling hydration of the materials during the test. Here we describe the design of a microfluidic platform for nanoindentation that facilitates continuous hydration of hydrogel samples and high throughput nanomechanical testing. We will show data from both stress relaxation and creep experiments on synthetic, hydrated biomaterials and tissues. We are also able to show the mechanical changes of these materials as a function of hydration levels and pH changes at the nano and microscale. In addition, we show data to validate the materials properties determined from nanomechanical

testing by complementary testing using macro and nano dynamic mechanical analysis. Finally, data from both test methods are fitted to phenomenological models for viscoelastic materials.

3:30 PM *R2.6/Y2.6

The effect of TGF-βbeta and glucocoticoid signaling on local mechanical properties of mouse bone. Mehdi Balooch[1], Sally J. Marshall[1], Grayson W. Marshall[1], Guive Balooch[1], Nancy Lane[2] and Wei Yao[2]; [1]UCSF, San Francisco, California; [2]SFGH, San Francisco, California.

Growth factor and hormone signaling can drastically affect the process of hard tissue formation, e.g. signaling molecules that have a large affect on bone formation include Transforming Growth Factor-β (TGF-β) and Glucocorticoids(GC). TGF-β has a vital and complex role in bone. TGF-β binds its cell-surface receptor to activate Smad3, a transcription factor that regulates the expression of defined genes, that determine osteoblast differentiation. However the effect of TGF-β on bone matrix quality is less clear. Excess glucocorticoids (GC) frequently leads to osteoporosis which is associated with increased fracture risk. This study assessed the effect of altered TGF-β signaling and GC excess on the intrinsic mechanical properties of mice bone. For the GC studies, we administered 1.4 mg/kg prednisolone to 6-month-old Swiss-Webster mice for 21 days. For TGF-β studies, transgenic mouse models with altered TGF-β signaling, ranging from 16-fold (D4 mice) and 2.5-fold (D5 mice) overexpression of TGF-β in bone, to decreased TGF-β signaling due to expression of a dominant negative TGF- receptor in bone (E1 mice) and targeted deletion of the Smad3 gene (Smad3 -/- and Smad3 +/- mice) were evaluated. Atomic force microscopy (AFM)/nanoindentation with stiffness mapping capability was utilized to assess the local bone quality. Raman microspectroscopy was performed to evaluate mineral and collagen content locally. Mice treated with GC had decreased serum osteocalcin in the lumbar vertebrae (LVB) compared to GC naive mice. This change in GC treated mice was accompanied by decreased bone formation (35%) and increased osteocyte apoptosis compared to GC naive controls (56%). Compared to GC naive mice, elastic modulus assessed across the trabecular bone regions was significantly reduced around osteocyte lacunae in GC treated mice (67%), independent of osteocyte apoptosis. Raman microspectroscopy of bone matrix/mineral around the osteocyte lacunae yielded a significant decrease in phosphates/organic content in GC treated mice compared to GC naive (36%). The findings provide evidence that GC-induced bone fragility could arise from changes associated with the osteocyte lacunae that alter bone strength Mice with elevated TGF-β signaling had on the average up to 23% lower elastic modulus and hardness relative to wild-type littermates. However, stiffness mapping revealed the existence of significant texturing in elastic modulus, ranging from 15 to 40 GPa. In contrast, mice in which TGF-β signaling was impaired (E1, Smad3 +/-, Smad3 -/-) had up to 54% increased elastic modulus and hardness, with no detectable texturing in elastic modulus. Though both have decreased TGF-β signaling, E1 mice are osteopetrotic whereas Smad3 -/- mice are osteopenic. In conclusion, we have provided evidence that growth factor and hormone signaling define bone intrinsic mechanical properties that, in turn, lead to changes in fracture resistance and overall bone matrix quality.

4:00 PM R2.7/Y2.7

Elastic Modulus of Dental Enamel: Effect of Enamel Prism Orientation and Mineral Content. Virginia Lea Ferguson[1,2], Alan Boyde[3] and Andy J. Bushby[2]; [1]Department of Aerospace Engineering, University of Colorado, Boulder, Colorado; [2]Department of Materials Science and Engineering, Queen Mary, University of London, London, United Kingdom; [3]School of Medicine and Dentistry, Queen Mary, University of London, London, United Kingdom.

Nanomechanical properties of mineralized tissues are determined by two main factors: microstructural tissue organization and relative composition of organic, mineral, and water phases. We combine nanoindentation and quantitative backscattered electron (qBSE) imaging to understand how these competing factors influence material properties at the ultrastructural and tissue level. Equine tooth enamel provides an ideal configuration to study the combined effects of enamel prism orientation and mineralization. Equine teeth undergo constant wear and growth thus necessitating longitudinally graded mineral content that increases with enamel maturity towards the biting surface. Hunter-Schreger bands (HSBs) extend from the dentino-enamel junction to the enamel surface in a direction perpendicular to the long axis of the tooth. Prisms within one band lie parallel to each other and at an angle to prisms in adjacent bands thus allowing investigation of crystallites in varying orientations. An equine (2-year-old) tooth, embedded in poly-methylmethacrylate, was sectioned longitudinally, polished, and carbon coated. qBSE images were collected to survey the tooth and for image analysis of prism geometry and mineralization level. Nanoindentation arrays measured elastic modulus in a 3.5 cm long array (500μm spacing) that extended from newly formed to fully mature enamel and in a tight array of indent sites (5μm spacing) over six partially mineralized HSBs. A relationship between the mineralization and modulus is presented which shows that elastic modulus increases dramatically as remaining pore spaces, located in regions of already highly mineralized enamel, are filled. In fully mature enamel, where modulus values exceed 80 GPa, prism orientation causes small perturbations (<1.5 GPa) in modulus values but remains a major contributor to enamel stiffness. Indentations spanning HSBs in immature, poorly mineralized enamel yield modulus values that vary with prism orientation in a sinusoidal-like pattern: transversely oriented prisms (11 GPa) are >2x stiffer than longitudinal prisms (4.5 GPa). We relate this to the packing of the mineral crystallites and organization of the pore spaces. In enamel, the high elastic modulus results largely from its sophisticated ultrastructural organization. Elucidating the ultrastructure of dental enamel will add both to our understanding of mineralized tissues and advance the development of novel biomimetic materials.

4:15 PM R2.8/Y2.8

Contribution of Collagen, Mineral, and Water Phases on Nanomechanical Properties of Bone. Amanpreet Kaur Bembey[1], Vanessa Koonjal[1], Virginia L. Ferguson[2], Andrew J. Bushby[1] and Alan Boyde[3]; [1]Department of Materials, Queen Mary University of London, London, United Kingdom; [2]BioServe Space Technologies, Engineering Centre, University of Colorado, Boulder, Colorado; [3]School of Medicine & Dentistry, Queen Mary University of London, London, United Kingdom.

Mechanical properties of bone are a consequence of the interaction between mineral, collagen and water. Mechanisms by which collagen orientation and mineral content influence mechanical properties of bone are poorly understood. Storage and preparation methods influence measurements of bone mechanical properties. Nanoindentation is a powerful method to examine mechanical properties of bone at the microstructural scale. Surface effects complicate nanoindentation of physiologically relevant bone samples. Thus, most studies examine dried, embedded, or included bone. To date, mechanical properties of mineral or collagen at the nano-scale are poorly defined. Beams of equine cortical bone were prepared to examine effects of dehydration and embedding and to study contribution of collagen and mineral to nano-scale material properties. Six beams were tested: untreated (hydrated); dehydrated in air, 100% ethanol; or embedded in poly-methylmethacrylate (PMMA) for one normal, one decalcified, and one deproteinated bone sample. Elastic modulus was obtained by nanoindentation using spherical indenters transverse and longitudinal to the bone axis. Dynamic mechanical analysis (DMA) data was obtained for same samples corresponding to longitudinal direction (AJ Bushby et al., JMR 2004). Statistical comparisons were performed using Student's t-test, α=0.05. Nanoindentation is normally relatively insensitive to anisotropy. Untreated bone did not demonstrate significant difference between two orientations. However, dehydration of bone in 100% ethanol emphasised anisotropy of the bone structure with mean elastic modulus increasing 37% from transverse to longitudinal direction. This anisotropy was reduced when subsequently embedded in PMMA. Influence of water on mechanical properties of bone is evident, but the manner in which liquid interacts with collagen and mineral is unclear. Deproteined sample showed more anisotropy than decalcified sample highlighting the importance of mineral crystal orientation. DMA and nanoindentation produced comparable results in the same orientation. Nanoindentation of bone in various conditions can reveal information about the ultrastructure of bone and role of the components including water.

4:30 PM R2.9/Y2.9

Nanoindentation of Bone in a Physiological Environment. Riaz Akhtar, Stuart Morse and Paul Mummery; School of Materials, University of Manchester, Manchester, Lancashire, United Kingdom.

Over the past decade nanoindentation has been established as an effective method to measure the mechanical properties of bone tissue at the nano scale. Although it is well documented that the mechanical properties of macroscopic bone specimens vary depending on whether the samples are tested dry or wet, nanoindentation is generally conducted on dehydrated bone tissue at room temperature, primarily because nanoindentation systems are extremely sensitive to changes in environmental conditions such as humidity and temperature. Other factors which tend to lead to spurious data when specimens are tested in liquid include surface roughness and swelling of cancellous bone, as well as small capillary forces acting on the indenter tip. In this study, these problems were overcome by using a specially constructed liquid cell with an extension piece that allowed the indenter tip to be submerged under 5 mm of liquid. A heating element with a temperature control unit was used to maintain testing temperature at 37°C. The liquid cell setup was calibrated using fused silica and single crystal [100] silicon. The mechanical properties of the calibration

materials were found to be similar when tested in dry and in physiological conditions. The elastic modulus and hardness of cortical and cancellous specimens, of both bovine and human bone, were investigated by using the nanoindentation liquid cell under physiological conditions. During initial testing in distilled water it was found that a hydrated oxide layer formed on the surface of trabeculae. However, subsequent testing in simulated body fluid allowed trabeculae to be probed reliably. The elastic modulus and hardness of bone tissue were found to decrease when dry specimens were rehydrated and tested in physiological conditions. Despite higher thermal drift, reproducible data have been obtained. It is suggested that nanoindentation in physiological conditions gives a better estimate of the mechanical properties of bone *invivo* at the nano scale rather than nanoindentation under conventional conditions.

4:45 PM R2.10/Y2.10

Effect of Mineral Content on the Nanoindentation Properties and Nanoscale Deformation Mechanisms of Bovine Tibial Cortical Bone. Kuangshin Tai[1], Hang J. Qi[2] and Christine Ortiz[1]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Cortical bone is a complex, load-bearing, hierarchical biocomposite material whose fine details of nano- to microscale structural organization, heterogeneity, composition, and mechanical properties are known to have profound effects on the macroscopic mechanical function and dysfunction of the tissue. Mineral content is one critical parameter affecting mechanical performance that varies with age, disease, and injury. In this study, a combination of nanoindentation, tapping mode atomic force microscopy (TMAFM), scanning electron microscopy (SEM), low-vacuum back-scattered electron detection, and Raman spectroscopy were used in conjunction with finite element analysis (FEA) and continuum elastic contact mechanical theory to assess the nanoscale structure-mechanical property relationships as a function of mineral content. Samples were cut from between the tibial metaphysis and diaphysis region parallel to the bone long axis, polished to a 0.05 m finish, and progressively demineralized with phosphoric acid and ethylenediaminetetraacetic acid. Nanoindentation experiments were performed on hydrated samples using a Berkovich diamond indentor (end-radius, RTIP=180nm) perpendicular to the osteonal axis up to a maximum force of 1000μN and depth of 500nm (containing a maximum of 31 type I collagen fibrils within the contact area). A nonlinear increase in elastic modulus with increasing mineral content was observed ranging from 2GPa (0 wt%) to 7-12GPa (58 wt%). 3D elastic-perfectly plastic FEA numerical fits to the nanoindentation data resulted in a yield stress, Y, that increased with increasing mineral content from a 4 wt% mineral sample (Y 0.2 +/- 0.08GPa) that was 33% less than that of the undemineralized sample. The characteristic 67nm axial banding for type I collagen fibrils was observed in TMAFM and SEM images for all partially and fully demineralized bone specimens. High resolution TMAFM images after nanoindentation allowed the direct visualization of nanoscale mechanisms of deformation. For the samples with low mineral content (wt%), the collagen fibrils within the indent region retained their banding and the integrity of their interfaces while conforming to the probe tip geometry up until maximum loads of 1000μN. At higher maximum loads of 7000μN, the collagen banding was destroyed in a localized region at the probe tip apex, suggesting mechanical denaturation. The undemineralized sample shows flattening of topographical features and pileup along the edges of the indent region at maximum loads of 500μN possibly due to a pressure induced structural transition of the mineral component. FEA simulations of these experiments reveal that at a maximum load of 1000μN, the pressure ranges up to 520MPa, which is close to the pressure required for phase transition in sintered, synthetic dense HA. These different mechanisms are thought to contribute to an overall transformation toughening mechanism originating at the nanoscale level.

SESSION R3/Y3: Joint Poster Session: Nanomechanics and Tribology of Biological Materials
Chairs: David Bahr, Yang-Tse Cheng, Norbert Huber, Adrian Mann and Kathryn Wahl
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

R3.1/Y3.1

Impedance Spectroscopy and Nanoindentation of Fuzzy Conducting Polymer Films on Neural Prosthetic Devices. Junyan Yang[1], David Martin[1] and David Martin; [1]University of Michigan, Ann Arbor, Michigan; [2], University of Michigan, Ann Abror, Michigan.

Microfabricated electrodes are being actively developed for the direct communication with neurons. We have been investigating the use of conducting polymer films for improving the long-term performance of these devices. By correlating measurements of probe electrical properties with surface morphology we have found that maximizing the effective surface area of the electrode coating makes it possible to minimize the electrical impedance. Nanoindentation allows for precise measurements of the mechanical properties of the thin polymer films as a function of their morphology and thickness. The micromechanisms of plastic deformation can be evaluated by correlating the indentation response with microstructural studies of the polymer before and after deformation. In this report, the electrical and mechanical properties of thin, fuzzy conducting polymer coatings on the neural prosthetic devices have been characterized by using impedance spectroscopy and nanoindentation. We found that the effective stiffness and electrical properties of the conducting polymer films varies with thickness and morphology. Our results reveal that for conducting polymers PPy and PEDOT the minimum impedance correlates well with the mechanical properties. In this series of materials, the films first become softer and rougher and then stiffen and get more dense as the polymerization continues. The lowest impedance films are also those that have the softest, most compliant mechanical response. This is consistent with the interpretation that the high surface area of the films promotes the most facile charge transport. This information provides clues for improving the long-term performance of these electrodes in-vivo.

R3.2/Y3.2

Aromatic Thiols and Plant Sterol Derivatives as Friction Modifiers. M. Ruths[1], S. Lundgren[1,2], K. Boschkova[1] and K. Persson[1]; [1]YKI, Institute for Surface Chemistry, Stockholm, Sweden; [2]Dept. of Chemistry, Surface Chemistry, Royal Institute of Technology, Stockholm, Sweden.

Aromatic molecules are less flexible than alkanes and have more complex intermolecular interactions, which makes their lubricating properties interesting both from a fundamental and from a practical point of view. Friction force microscopy (FFM) and the surface forces apparatus technique (SFA) were used to study the boundary friction of single- and multicomponent self-assembled monolayers of aromatic thiols and silanes, plant sterol derivatives, and rosin acids. At conditions of low adhesion, good agreement was found between friction coefficients measured with the two techniques despite the large differences in the contact areas, forces and pressures. In mixed aromatic thiol monolayers, friction coefficients and transition pressures are intermediate to the ones found in monolayers of pure compounds, suggesting a way to tune the friction response by varying the composition.

R3.3/Y3.3

Effect of Flour on Mechanical Properties of Teeth Demineralized by Use of Othodontic Appliances. Claudia Centeno[2], Ulises Ruiz[2], Oscar Contreras[1] and Enrique C. Samano[1]; [1]CCMC-UNAM, San Ysidro, California; [2]Facultad de Odontologia, UAEM, Toluca, Mexico.

The risk of dental caries increases with the use of orthodontic appliances, and it does not only depend on patients's oral hygiene. Caries causes that the enamel of teeth demineralizes close to the orhodontic bracket. The hardness of teeth consequently decreases, becoming brittle and loose. The type of adhesive used to fix orthodontic brackets might reduce or not enamel demineralization. Previous studies have shown that a resin-modified glass ionomer (RMGI) cement and fluoride varnish might inhibit demineralization. The purpose of this work is to evaluate the effect of a fluoride-releasing cavity varnish on mechanical properties of dentin and enamel in regions adjacent to orthodontic brackets bonded with RMGI and composite resin cements. The demineralization effect on teeth was assesed by measuring hardness and relative elastic modulus on dental pulp, dentin and enamel around the bracket area by nanoindentation methods. Nanoindentation was performed using a TriboScope from Hysitron. For this purpose two sets of samples were prepared: one set with no orthodontic treatment and the other one with orthodontic treatment using the adhesive already described. A relationship between mechanical properties and fluor content is found. The amount of fluor in the teeth was obtained by X-ray photoelectron Spectroscopy (XPS). The morphology of the samples is determined in situ by means of the TriboScope in the imaging mode.

R3.4/Y3.4

Variation of Ultrastructure and Nanomechanical Properties of Individual Chondrocytes with an Increasingly Thick Pericellular Matrix. Laurel J. Ng[1], Alan Grodzinsky[1,2,3] and Christine Ortiz[4]; [1]Biological Engineering, MIT, Cambridge, California; [2]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [3]Mechanical Engineering, MIT,

Cambridge, Massachusetts; [4]Material Science and Engineering, MIT, Cambridge, Massachusetts.

Chondrocytes make up <10% of cartilage volume and are solely responsible for the synthesis, assembly, and catabolism of the extracellular matrix (ECM) molecules. A mechanical property gradient exists from the cell (elastic modulus, E 1kPa) to its surrounding pericellular matrix (PCM, E 60kPa) to the bulk ECM (E 1MPa), which acts to regulate the amount of cell deformation caused by external loads applied to the tissue. The PCM, in particular, plays a role in the both biomechanical and biochemical cellular function, modulating the strains felt on the cell during compression and controlling the immediate environment surrounding the cell. Our objectives in this study were (1) to directly visualize the in vitro synthesis of ECM macromolecules from individual chondrocytes and the evolving ultrastructure of the PCM via tapping mode atomic force microscopy (TMAFM) imaging and (2) to correlate the production of ECM by individual chondrocytes with changes in the nanomechanical properties of the cell-PCM composite via nanoindentation, both as a function of time in culture. To address the first goal, chondrocytes isolated from bovine articular cartilage were cultured and released from 3mm diameter alginate beads at intervals over one month, deposited onto freshly cleaved mica, and visualized using TMAFM in ambient conditions. At day 4 of the culture, individual collagen fibrils were observed emanating from the cell surface (88±9nm diameter, 58±6nm characteristic banding periodicity). At day 6 of the culture, a distinct halo of PCM (thickness 9μm) was present and by day 18, a dense, homogeneous, network of collagen fibrils was clearly visibly. For the second objective, culture-released cells were deposited onto silicon plates containing pyramidal 20μm diameter wells, each of which held individual live chondrocytes in place for both TMAFM and single cell nanoindentation experiments in fluid as a function of culture time. This method also allows for visual confirmation of chondrocyte phenotype and size measurement (and therefore PCM growth) of each cell that is being studied. Nanoindentation using Si3N4 pyramidal probe tips (radius 50nm) showed a distinct increase in compressive stiffness with culture time due to the growing PCM, as reflected by an increase in the slope of the force vs. indentation depth curves. The indentation data exhibited nonlinear hysteretic behavior, indicating the cell and its PCM are viscoelastic or perhaps poroelastic. Due to the small probe tip end radius, contact is likely made with individual molecular components of the PCM (e.g., proteoglycans and collagen fibrils) and not representative of bulk PCM properties. To measure the larger scale material properties of the PCM, further nanoindentation experiments are currently underway using μm-sized colloidal tips. Finite element modeling is being used to interpret this data and predict nanomechanical properties such as elastic and viscoelastic properties such as storage and loss moduli.

R3.5/Y3.5

Effects of Osteopontin on Nanomechanics and Microstructure of Mouse Bones. Beril Kavukcuoglu[1], Courtney West[3], David Denhardt[2] and Adrian Mann[1,3]; [1]Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey; [2]Cell Biology and Neuroscience, Rutgers University, Piscataway, New Jersey; [3]Biomedical Engineering, Rutgers University, Piscataway, New Jersey.

Osteopontin (OPN), a phosphorylated glycoprotein, is among the most abundant non-collageneous bone matrix proteins produced by osteoblasts and osteoclasts. OPN has been implicated in bone formation, resorption and remodeling, however, previous studies have presented contradictory results regarding the effect of OPN on the mechanics and microstructure of bone. This study has used nanoindentation to identify local variations in elastic modulus and hardness of osteopontin deficient (OPN -/-) and wildtype control (OPN+/+) mouse bones. Specifically, the study has looked at changes in the bones mechanical properties with the mouse age, background and sex. The mechanical properties have been correlated with changes in the local structure of the bone as observed with SEM, FTIR , XRD and micro-Raman. Cortical sections of femurs from 3 week old and 6 month old mouse bone were tested and compared. The results suggest that there are large, abrupt variations in mechanical properties across the femur radial section for 3 week old mouse bone. The hardness (H) drops down significantly towards the inner and outer sections resulting in a standard deviation of 2.6 GPa with a mean H=5.1 GPa. In order to obtain statistically comparable data only the hardness measurements taken from interior area, which show a standard deviation of 1.7 GPa with mean H=6.5 GPa are taken into consideration. The hardness of the 6 month old mouse bone has a standard deviation of 0.25 GPa and a mean H=1.4 GPa. The hardness along the radial axis of the 6 month old was found to be quite homogeneous. Just like hardness, elastic modulus also shows abrupt variations along the radial axis of the young mouse bone whereas it remains quite constant for the 6 month old. Therefore we conclude that the mechanical properties of the mouse bones decrease substantially with maturity, but statistically hardness and elastic modulus are more homogeneous in mature bones than young ones. We found a similar variation in both OPN-/- and OPN+/+ bones, but the magnitude of the mechanical variation appears to depend not only on the age, but also the presence or absence of OPN. The mechanical variations correlate with changes in the degree of mineralization and crystallinity of the bone as revealed by the structural analysis. That is, high mineral content and high crystallinity corresponds to regions of increased hardness and stiffness. The results for OPN-/- and OPN+/+ mouse bones are particularly important as control of OPN activity has been postulated as a potential treatment for bone pathologies that exhibit a change in the bone mineralization, such as osteoporosis, osteopetrosis and Paget's disease. Understanding the effects of OPN on bone mechanics is a vital step in the development of these new treatments.

R3.6/Y3.6

Spatially Dependent Mechanical Properties of Rat Whiskers for Tactile Sensing. Elizabeth K. Herzog[2,1], David F. Bahr[1], Cecilia D. Richards[1], Robert F. Richards[1] and David M. Rector[3]; [1]Mechanical and Materials Engineering, Washington State University, Pullman, Washington; [2]Materials Engineering, Purdue University, West Lafayette, Indiana; [3]Veterinary and Comparative Anatomy, Pharmacology, and Physiology, Washington State University, Pullman, Washington.

A new generation of sensors based on biologically inspired whisking action will help determine the presence and location of solid objects and fluid vortices similar to mechanisms used by whisker bearing animals such as rats and seals. A key to this system is the mechanical response of the whiskers to applied forces, which will be impacted by the elastic properties of these biologically inspired structures. To determine the effectiveness of biological whisking structures the elastic, viscoelastic, and plastic properties of whiskers from laboratory rats were determined. By using dynamic nanoindentation, we demonstrate that mechanical properties are essentially uniform by cross section over an entire whisker, but vary longitudinally from the whisker base (a 3.9 GPa elastic modulus) to the tip (a 3.1 GPa elastic modulus). Several recent studies show propagation of high frequency information through whiskers that are tuned by their physical properties, and have measured an average elastic response of approximately 3.5 GPa. In order to fully understand and model these properties, this study demonstrates the need for a more complex whisker structure than previously assumed.

R3.7/Y3.7

Nano-mechanical Testing of a Biological Protective Coating of a Visco-elastic Material. Niels Holten-Andersen[1], Nelle Slack[2], Frank Zok[3] and Herbert Waite[1]; [1]BMSE, UCSB, Santa Barbara, California; [2]Veeco Metrology, LLC, Santa Barbara, California; [3]Materials, UCSB, Santa Barbara, California.

The holdfast structure of mussels, the byssus, is a structure with unique visco-elastic mechanical properties evolved to withstand the challenges of the turbulent saline environment of the intertidal zone. Each byssal thread consists of three functional domains: the glue in the plaques which bonds the thread to a variety of hard surfaces, the fibrous collagenous core which connects with the glue and resists the applied loads of waves, and, the topic of this investigation, the coating covering all parts of the byssus. The major protein of the coating is Mussel foot protein-1 (Mfp-1). A large database in biochemistry, surface chemistry, molecular biology and covalent modification exists on Mfp-1 and it has traditionally been considered the best known of the mussel adhesive proteins. Mfp-1 is the active ingredient in a broad spectrum cell and tissue attachment factor and analogs have been used to anchor tethered pegylated polymers to implant surfaces thereby successfully establishing nonfouling implant surfaces in cell culture. However, ironically Mfp-1 is not the adhesive but rather the coating of the mussel byssus. In the distal portion of the thread the coating has a micron-sized knob-like consistency. This is the part of the thread outside the mussel shell and hence we speculated that it endows the threads with protection against abrasion. The mechanical properties of the coating have been investigated with the use of nano-indentation and the coat was found to confer mechanical protection of the thread interior due to a significantly higher hardness. Our data furthermore indicate that the thread distal coating is a metal-protein composite. The proteinaceous matrix of the distal coat additionally contains the elements Fe, Si, Al and Br. However, the relative distribution and specific form of these elements in the coat are currently unknown. Their potential correlation with the knob-like structure of the distal coat and their role in the coats mechanical behavior is intriguing and has been further investigated. Finally despite its apparent hardness, the distal coating accommodates strains of up to 70%. Current data indicate that the distal coat rearranges without loss of integrity in accordance with the tension experienced by a thread. A fundamental understanding of how the molecular structure and function are adaptively related in the mussel byssus coating would therefore

greatly assist and accelerate the intelligent design of unique bio-inspired coatings which are durable, protective and extensible.

SESSION R4: New Methods and Time Dependent Characterization
Chairs: Graham Cross and Mark Van Landingham
Tuesday Morning, November 30, 2004
Room 202 (Hynes)

8:30 AM *R4.1
New Nano Indentation Experimental Techniques and Modeling Procedures. Warren Carl Oliver[1], Eric Herbert[1], Peirre Morel[1] and Jonathan C. Doan[2]; [1]Nano Instruments Innovation Center, MTS Corporation, Oak Ridge, Tennessee; [2]Reflectivity, Sunnyvale, California.

A new probe scanning system developed to provide as yet unattainable precision and accuracy in images and probe positioning capabilities will be presented and applied to a biological sample as well as a new MEMS testing structure. Images and mechanical tests of red blood cells will be presented and discussed. The MEMS structure considered will be an end supported, free standing film strip that is forced to undergo an instrumented stretching process. The resulting load displacement information will be analyzed with a simple membrane stretching model. Finally, several analysis model for indentation load displacement information will be discussed.

9:00 AM R4.2
On the Measurement of Creep by Nanoindentation with Continuous Stiffness Techniques. Andrei Rar[1,2], David L. Goldsby[3], Terry E. Tullis[3] and George M. Pharr[1,2]; [1]Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Materials Science and Ehgineering, The University of Tennessee, Knoxville, Tennessee; [3]Department of Geological Sciences, Brown University, Providence, Rhode Island.

Measurement of material creep parameters by means of nanoindentation using continuous stiffness techniques avoids problems associated with thermal drift that often plague creep measurements based on the time dependence of the indentation depth alone (1,2). Problems with thermal drift are much less severe during continuous stiffness measurements because the contact stiffness can be measured over a very short time period, typically less than one second, during which displacements due to thermal drift are minimal. The determination of the time dependence of the indentation depth from the stiffness data relies on the well-known relation between contact stiffness and the square root of the contact area. For pyramidal indenters, the true indentation contact depth must be proportional to the contact stiffness, leading to the assumption that indentation depth is also proportional to the contact stiffness. In this investigation, we checked this assumption using data obtained from experiments on several relatively soft materials (e.g., Al, epoxy, PMMA) in which creep displacements are much greater than those due to thermal drift. Initial results suggest that after initial load application or following a load change, the relative change in contact area may be much greater than that expected from the relative change in indentation depth. Possible reasons for the observed differences and their influences on the interpretation of creep data are discussed. Research at the Oak Ridge National Laboratory SHaRE User Center was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. (1) T. P. Weihs and J.B.. Pethica, Mat. Res. Soc. Symp. Proc. **246**, 325 (1992). (2) D. L. Goldsby, A. Rar, G.M. Pharr, and T. E Tullis, J. Mater. Res. **18**, 357 (2004).

9:15 AM R4.3
Multiple Frequency Nanoindentation Testing.
Anthony Craig Fischer-Cripps, Industrial Physics, CSIRO, Lindfield, New South Wales, Australia.

A new method of dynamic nanoindentation testing is introduced. The work describes a method whereby the storage and loss modulus of viscoelastic solids can be determined using a multi-frequency dynamic oscillatory motion mode of deformation. In this method, the applied load is modulated by a pseudo-random force signal comprising multiple frequencies. A Fourier analysis is then used to deconvolute the signal into frequency dependent values of storage and loss modulus for the specimen material as a function of frequency. The instrument response is cancelled by the use of a reference transfer function using an equalization process. Established modeling equations can then be used to extract the modulus of elasticity and the viscosity of the specimen material.

9:30 AM *R4.4
Recent Advances in Nanomechanical Characterization by Nanoindentation. Oden L. Warren, Hysitron, Inc., Minneapolis, Minnesota.

Nanomechanical characterization by nanoindentation typically involves simple quasistatic testing at a few sites per test specimen of moderate to high elastic modulus and indentation hardness. However, recent advances in both hardware and software technologies now enable measurement speed suitable for high-throughput screening of combinatorial phase diagrams as well as non-traditional but still quantitative techniques such as nanoscale dynamic mechanical analysis, complex modulus imaging, probe-sample adhesion testing under rigid displacement control, and highly-localized acoustic emission monitoring concurrent with nanoindentation. The first three of these newer techniques are compatible with soft, compliant, and often viscoelastic materials, and the last is useful for fingerprinting various classes of transient deformation events. This presentation focuses on a number of case studies that nicely illustrate the state-of-the-art in nanoindentation instrumentation and methodology. Some examples are given from the perspective of a generalized force-displacement tool endowed with high sensitivity and accuracy rather than from the viewpoint of classical nanoindentation testing.

10:30 AM *R4.5
Methods for the Measurements of Viscoelastic Functions in Both Time and Frequency Domains Using Nanoindentation. Hongbing Lu, Bo Wang and Gang Huang; School of Mechanical and Aerospace Engineering, Oklahoma State University, Stillwater, Oklahoma.

Methods are presented to measure viscoelastic functions defined in linear regime in both time domain and frequency domain. In time domain, we present methods to measure the creep functions through direct differentiation methods using load/displacement data and material parameter extraction methods by fitting load-displacement relation under condition that the Poisson's ratio is assumed constant. We also present a method to measure two independent viscoelastic functions for an isotropic material using nanoindentation. Finding two independent material functions through nanoindentation is necessary for polymers with glass transition temperature near test temperature, and for new materials with unknown Poisson's ratio. In frequency domain, we present a method to measure complex viscoelastic function under cyclic loading condition. Three polymers are used in validation, they are: polymethyl Methacrylate, polycarbonate and polyurethane. Nanoindentation results on viscoelastic functions are compared with results from uniaxial tests or dynamic mechanical analysis (DMA) tests to validate the nanoindentation techniques. The methods are then used in characterizing mechanical behavior of some biomaterials and (CNT, nanoclay) nanocomposites. The methods presented are appropriate for small amounts of viscoelastic materials such as nanocomposites, polymeric films/coatings and biomaterials in linearized viscoelastic regime.

11:00 AM R4.6
Displacement Modulation Based Dynamic Nanoindentation for Viscoelastic Material Characterization. Sehaj P. Singh[1], Raman P. Singh[1] and James F. Smith[2]; [1]Department of Mechanical Engineering, Stony Brook University, Stony Brook, New York; [2]Micro Materials Ltd., Wrexham, United Kingdom.

Nanoindentation based techniques for measuring quasi-static properties like hardness and Young's modulus are well developed for elastic materials. Hardness can be obtained from the peak valued of applied load and the contact area at that load, and Young's modulus can be obtained from the slope of the unloading curve. However, quasi-static indentation of viscoelastic polymers is questionable at best due to time dependent material response. Dynamic nanoindentation techniques offer a promising alternative as they provide measurements of both storage and loss and involve significantly decreased testing time by examining properties over a range of frequencies rather than extended time. Currently, the most common technique used for dynamic nanoindentation is based on force modulation, in which dynamic excitation is provided using a low magnitude oscillating force superimposed onto the overall quasi-static force signal during the loading process. The displacement response is then measured at the same frequency as the applied oscillating force and the resulting phase lag is related to the dynamic stiffness and damping of the material. In the current work, a new displacement modulation based dynamic nanoindentation technique is demonstrated for viscoelastic material characterization. It is shown that the use of displacement modulation results in a more robust approach that is cabable of viscoelastic characterization over a greater frequency range as compared to the technique based on force modulation. Tests are carried out on the NanoTest Platform (Micro Materials Ltd., Wrexham, UK) using a special dynamic nanoindentation module. This module includes a piezoelectric sample holder for providing the oscillation and a lock in amplifier for recording the phase difference between the input oscillation and the output response of the indenter

that is in contact with the sample. A new calibration procedure, which involves the use of a cantilever spring, is employed to determine the elastic stiffness and damping characteristics of the testing frame as a function of excitation frequency. Testing of the samples involves conducting cyclic load-partial unload indentation with increasing load and a dwell period at the end of each load cycle. Oscillation data is collected at each dwell period and a phase difference versus plastic depth of indentation curve is obtained. A curve fit of this data with the theoretical solution yields the contact stiffness and damping, which are then used to obtain the storage and loss modulus of the material. For the verification of the proposed testing procedure, tests are carried out on two materials: aluminum, which has a negligible loss modulus, and an epoxy, which has a significant loss modulus, at various frequencies ranging from 10 to 80 Hz and the observations are found to be in very good agreement with conventional bulk measurements.

11:15 AM R4.7
On the Measurement of Material Creep Parameters by Nanoindentation. J. A. LaManna[1], W. C. Oliver[2] and G. M. Pharr[1,3]; [1]Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; [2]MTS Systems Corp, Nano Instruments Innovation Center, Oak Ridge, Tennessee; [3]Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, Tennessee.

Previous studies of how material creep parameters can be measured by nanoindentation testing have focused mostly on how one can determine the stress exponent for creep, n, and the activation energy for creep, Q_c. However, a more complete characterization requires that the material constant A in the uniaxial creep equation, where the uniaxial strain rate is equal to $A\sigma^n$ (σ is the uniaxial stress), also be evaluated from the nanoindentation data. Here, we address this issue by performing simple nanoindentation creep experiments in amorphous selenium at temperatures above and below the glass transition. At the higher temperatures, the material exhibits a simple linear viscous creep behavior that is load history independent. This allows the parameter A to be determined from the nanoindentation load-displacement-time data by means of a theoretical solution. Values of the parameter A measured in nanoindentation tests are compared to independent measurements obtained in uniaxial tension creep experiments.

11:30 AM R4.8
Determining the Energy and Volume of Individual Defects by High Temperature Nanoindentation. Christopher A. Schuh and Alan C. Lund; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Incipient plasticity during nanoindentation is often associated with the discrete production of defects, most notably dislocations, cracks, and shear bands. The athermal mechanics of defect nucleation under a nanoindenter have received much attention, but recognizing that there is a significant contribution of thermal activation to these processes allows a new, statistical description of incipient plasticity. This approach offers a convenient and robust technique to assess the activation volume of individual defects, and when coupled with elevated temperature nanoindentation experiments, can also assess activation free energies. This talk will present our progress in extracting the properties of individual dislocations in metals and ceramics, as well as shear band characteristics in metallic glasses.

11:45 AM R4.9
High Temperature Deformation of AlN/CrN Multilayers using Nanoindentation. Finn Giuliani[1], A. Goruppa[2], S. J. Lloyd[1], D. Teer[2] and W. J. Clegg[1]; [1]Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; [2]Teer Coatings Ltd., Droitwich, United Kingdom.

Substantially increased hardnesses have been observed in nitride multilayers with layer thicknesses of the order of 10 nm. The aim of this paper is to investigate whether such effects can also be observed at elevated temperature and to study the effects of temperature on the deformation patterns under the indent. The hardness of AlN/CrN multilayer structures with wavelengths varying from 6-200 nm has been studied at temperatures from room temperature up to 750°C. These measurements have been correlated with changes in deformation patterns using cross-sectional transmission electron microscopy, where sections have been prepared directly through the indents, and the changes in nature of flow of material using the layers as internal markers.

SESSION R5: Polymeric Materials
Chairs: Nancy Burnham and Hongbing Lu
Tuesday Afternoon, November 30, 2004
Room 202 (Hynes)

1:30 PM *R5.1
Molecular mobility and confined plasticity in ultrathin polymer films. Rene M. Overney and Scott Sills; Chemical Engineering, University of Washington, Seattle, Washington.

Lateral force microscopy (LFM) has come a long way to develop into a widely used chemically distinctive nano-tool and a truly molecular/atomic scale tribological force apparatus. With its nanometer-sharp tip, the LFM cantilever, sensitive to sub-nanonewton forces, has shown to be able to probe a single surface potential well, and to address the hopping dynamics governing sliding friction involving solids and "interfacially cooled" liquids. That it is actually possible to infer truly material intrinsic properties with the LFM, i.e., inter- and intra-molecular relaxations, is rather unexpected and discussed in this paper. An elaborate LFM analysis is introduced as a method that provides the crucial link between spectroscopic analysis and nanoscopic thermomechanical probing. It will be demonstrated that activation energies related to molecular mobilities in the vicinity of thermal relaxation processes can be deduced. In addition, the correlation length of the cooperative molecular motion near the glass transition is determined, and this, for the first time, model-independent. In this talk, also substrate constraints in ultrathin polymer films will be addressed, and its impact on high strain rate nano-indentations. This particular study is motivated by recent advances in ultrahigh density thermomechanical data storage, a novel recording scheme intended to circumvent the superparamagnetic limit associated with magnetic storage. The non-monotonic rheological property gradient in ultrathin polymer films (thickness < 100 nm), will be particularly emphasized for the high strain-rate nano-indentation process that diverts from its bulk counterpart.

2:00 PM R5.2
On Factors Affecting the Extraction of Elastic Modulus by Nanoindentation of Organic Polymer Films. Francesca Iacopi[1], Mourad Laknin[1,2], Danielle Vanhaeren[1] and Sywert H. Brongersma[1]; [1]IMEC, Leuven, Belgium; [2]Faculte' des Sciences et Techniques, Universite' d'Aix et Marseille, Marseille, France.

In this work we carry out a detailed analysis of nanoindentation in Continuous Stiffness Mode (CSM) on a family of aromatic thermosetting polymers with low molecular weight, developed as inter-layer low-k dielectrics for interconnects. The values reported in literature for elastic modulus of such organic polymer films as extracted from nanoindentation can vary considerably [1, 2, 3]. Also, we found that values of elastic modulus for polymer films as extracted from Surface Acoustic Waves can be up to 50% lower than those extracted from indentation, even for a film thickness range where the well-known substrate is not yet observed. This analysis indicates that beyond issues related to the precise positioning of the surface upon indentation (typical for all soft and thin supported films [4]), some parameters determining the dynamics of the force application during load and unload such as the frequency of the continuous stiffness measurement, the actual strain rate (and consequently the surface approach velocity), and the peak hold time before unload can lead up to 20% difference in the extracted values of elastic modulus. These variations appear more pronounced for organic films than for inorganic or hybrid materials. The reason for this appears related to viscoelastic behaviour, typical of organic films [5, 2]. On the other hand, artefacts from plastic deformation like extensive pile-up is shown to be significant only for indentation depths above 30% of the film thickness, even for films with hardness as low as 0.1 GPa. [1] S.J.Martin, J.P.Godschalx, M.E.Mills, E.O.Shaffer, P.H.Townsend, Advanced Materials 12 (23), pp.1769-1778, 2000. [2] F.Iacopi, S.H.Brongersma, K.Maex, Appl.Phys.Lett. 82 (9), 2003, 1380-1382. [3] L.Shen, K.Zeng, Microelectron.Eng. 71, pp.221-228, 2004. [4] S.H.Brongersma, 3rd European Symposium on nano-mechanical testing, 2003 Hueckelhoven, Germany. [5] J.Den Toonder, A.Van Dijken, V.Gonda, J.Beijer, K.Zhang, J.Waeterloos, L.Ernst, Electronic Components and Technology Conference (ECTC), May 3003, New Orleans, La.

2:15 PM R5.3
Viscoelastic Characterization of Polymers Using Dynamic Instrumented Indentation. Christopher C. White[1], Mark R. VanLandingham[2] and Peter L. Drzal[1]; [1]Building and Fire Laboratory, Polymeric Materials Group, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Weapons & Materials Research Directorate, ATTN: AMSRD-ARL-WM-MA, Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Dynamic nanoindentation was preformed on a cured epoxy, poly(methyl methacrylate), (PMMA), and two different crosslink density poly(dimethyl siloxane) (PDMS) samples. These samples are used to compare dynamic nanoindentation with classical rheological instrumentation measurements on polymeric samples in the glassy and rubbery plateau regions. Excellent agreement between bulk rheological data and dynamic nanoidentation data was observed for

the two glassy materials and the less compliant of the two PDMS samples. More divergent results were observed for most compliant PDMS sample. The theoretical foundation and historical development of the working equations for these two types of instrumentation will be presented and discussed. The major difference between nanoindentation and the more classical rheological instrumentation is in the treatment of the instrument-sample interface.

2:30 PM R5.4
Dynamic-Nanoindentation Analysis of Viscoelastic Materials. Jack E. Houston, Surface and Interface Sciences, Sandia National Laboratories, Albuquerque, New Mexico.

Understanding the unique properties of nano-phase materials requires analysis of the mechanical properties at the nano-scale. Since many such materials involve the inclusion of small particulates in a polymer matrix, it is important to be able to analyze the viscoelastic behavior of the matrix in the region adjacent to the particulates, the so called interphase region. Classic nanoindentation techniques have been applied to such studies and, more recently, scanning probes have demonstrated the potential to be very important for this type of analysis. However, such applications are made difficult by the critical role played by contact mechanics in the process and, at the nano-scale, the contact is not directly observable. In this presentation, dynamic indentation measurements, i.e., creep and relaxation, are demonstrated using the interfacial force microscope (IFM) applied to several viscoelastic polymer surfaces in order to demonstrate the potential for this type of analysis. The materials range from a hard polymer to a classic liquid solid or dilatant material–in this case Silly PuttyTM (trademark: Binney and Smith). This material is unusual because it exhibits elastic behavior over short experimental times (high Deborah numbers) and viscous properties over long times (low Deborah numbers). In addition, the critical role of adhesion, a factor often overlooked in nanoindentation measurements, is demonstrated through the use of both lyophilic and lyophobic tips. One of the advantages of the dynamic measurements is that, once linearity has been demonstrated, a subsequent Fourier analysis permits the frequency spectrum of both the real and imaginary components of the material compliance to be routinely obtained. This process is demonstrated by a direct comparison of the resulting frequency response for the dilatant material with that obtained from a more classical bulk measurement using an oscillating pendulum rheometer. While some of these demonstration results are not done at the true nano-scale, the discussion will include an assessment of the potential, and contact-mechanics difficulties, involved in proceeding to that regime. *Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy, National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:15 PM *R5.5
Indentation Creep and Relaxation Measurements of Polymers. Mark R. VanLandingham[1], Peter L. Drzal[2] and Christopher C. White[2]; [1]Materials Division, U. S. Army Research Laboratory, Aberdeen Proving Ground, Maryland; [2]Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

Instrumented indentation, sometimes referred to as nanoindentation, is increasingly being used to probe the mechanical response of polymeric materials. In contrast to traditional engineering materials (i.e., metals and ceramics) to which indentation techniques have most often been applied, the characterization of polymers by a single modulus or hardness values is often of limited value because of their viscoelastic nature. Additionally, polymers often behave in a nonlinear fashion at relatively small levels of strain, and their responses to tension, compression, or shear can be quite different. Thus, a number of challenges exist to applying instrumented indentation methods to polymeric materials. In this research, instrumented indentation is used to characterize the creep and stress relaxation responses of both glassy and rubbery polymers at room temperature using a variety of tip geometries. Indentation creep tests, in which a constant load is applied and held constant, and indentation stress relaxation tests, in which a constant displacement is applied and held constant, are used to measure creep compliance and stress relaxation modulus values, which were calculated based on a model of contact between a rigid indenter tip and a linear viscoelastic half space. Data from traditional solid rheology measurements are compared to the indentation data.

3:45 PM R5.6
Nanomechanical Quantification of Polymer Energy Absorption. Catherine A. Tweedie[1], James F. Smith[2] and Krystyn J. Van Vliet[1]; [1]Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Micro Materials Limited, Wrexham, United Kingdom.

Nanoscale contact experiments such as nanoindentation and scanning probe microscopy-enabled force spectroscopy are used increasingly to compare qualitatively the mechanical response of soft materials such as polymers. However, little has been reported on the quantification of the time- and temperature-dependent deformation of bulk and thin film polymers as this relates to the structure, physical properties and salient performance characteristics of these materials in service. Here, we present a new experimental approach and physical interpretation to quantify accurately the viscoelastoplastic properties and energy absorption potential of several bulk and thin film polymers through nanomechanical contact, and correlate these results with those obtained through micro- and macroscale mechanical analysis. We relate the molecular weight, molecular structure and glass transition temperature of structurally simple polymers to the mechanical response as a framework to quantify mechanical properties of structurally complex materials such as block copolymers, liquid crystals and nanocomposites.

4:00 PM R5.7
Instrumented Nanoindentation of Model Soft Elastomers and Adhesion Effects. Peter L. Drzal[1], Aaron M. Forster[2], Mark R. VanLandingham[3] and Christopher C. White[1]; [1]Building and Fire Laboratory, Polymeric Materials Group, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland; [3]Weapons & Materials Research Directorate, ATTN: AMSRD-ARL-WM-MA, U. S. Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Recent advances in instrumented nanoindentation techniques have provided the capability to measure dynamic mechanical properties of polymers over length scales that are inaccessible with conventional rheometry. However, nanoindentation of polymeric (and biological) materials with elastic moduli values less than 10 MPa still present significant challenges. The two primary challenges are static load signal resolution and tip-sample adhesion. Current static load sensitivities make the identification of the initial tip-sample contact point difficult and provide poor load resolution at indentation depths less than 2 microns. The uncertainty in the initial tip-sample contact adds significant uncertainty to the area function, A(hc), when applied to soft materials. While dynamic oscillation of the tip greatly improves the load sensitivity to the tip-sample contact and dynamic load resolution during the indentation, adhesion between the tip and surface becomes relevant as the modulus of the material decreases and can play a dominant role in the actual tip-sample contact area. A characteristic length over which adhesion affects the tip-sample interaction can be considered by determining the ratio of the thermodynamic work of adhesion to the elastic modulus (W/E). During the loading portion of an indentation measurement, where the dynamic oscillation measurements are typically evaluated, the thermodynamic work of adhesion establishes an upper limit of the driving energy to bring two surfaces together. Using a characteristic value of 50 mJ/m^2 and a modulus of less than 1 MPa, the length scale over which adhesion affects the indentation experiment can approach 500 nm. This characteristic length scale is significant relative to contact area and penetration depth during indentation. In fact, the elastic contact depth used to evaluate A(hc) area functions is no longer valid because the adhesive forces cause a deviation from the strictly elastic analysis. To address these issues, a series of model elastomeric poly(dimethyl siloxane) samples were made with a range of elastic moduli (10^5-10^7 Pa) by varying the crosslink density. Area function curves for a series of nanoindenter tips were determined optically with the use of a JKR-type apparatus. The optically determined area functions are then compared to those obtained from traditional methods to establish the bounds at which adhesion must be considered for accurate determination of mechanical properties.

4:15 PM R5.8
Comparative Evaluation of Different Dynamic Nano-indentation Techniques Used for Testing Polymeric Materials. Raman P. Singh[1], Mark R. VanLandingham[2] and Peter L. Drzal[3]; [1]Department of Mechanical Engineering, Stony Brook University, Stony Brook, New York; [2]Weapons & Materials Research Directorate, ATTN: AMSRD-ARL-WM-MA, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland; [3]Building and Fire Laboratory, Polymeric Materials Group, National Institute of Standards and Technology, Gaithersburg, Maryland.

Dynamic nanoindentation techniques, which involve the combination of conventional quasi-static depth-sensing indentation along with a small force or displacement modulation, can be used for quantitative measurement of time-dependent material properties such as loss and storage moduli and other viscoelastic characterization of polymeric and soft biological materials. However, the successful application of these techniques is highly dependent upon system modeling, instrument calibration, and testing analysis procedures. Slight differences in these experimental aspects have led to considerable variations in measured properties as a function of different testing

instruments and procedures. In the reported research, dynamic nanoindentation, using three different commercially available instruments, was employed to characterize a host of polymeric materials that exhibit viscoelastic response, including isotactic and syndiotactic poly-methylmethacrylate (PMMA), poly-dimethylsiloxane (PDMS) and an amine-cured bisphenol-F epoxy. The three instruments used, the Nano Indenter DCM (MTS Systems Corp., Oak Ridge, Tennessee), the TriboScope (Hysitron Inc., Minneapolis, Minnesota) and the NanoTest (Micro Materials Ltd., Wrexham, United Kingdom), differ in terms of applied modulation, system calibration, and testing and analysis procedures. The nanoindentation tests were conducted as a function of modulation frequency and the measured mechanical properties were compared with values obtained from conventional dynamic mechanical analysis (DMA). The results from this investigation have established that careful control of testing parameters, system calibration and analysis procedure is required to ensure consistent measurement of time-dependent material properties.

4:30 PM R5.9
Spherical Indentation Creep Following Ramp Loading.
Michelle L. Oyen, University of Minnesota, Minneapolis, Minnesota.

Depth-sensing indentation testing is a common way to characterize the mechanical behavior of stiff, time-independent materials but presents both experimental and analytical challenges for compliant, time-dependent materials. Many of these experimental challenges can be overcome by using a spherical indenter tip with a radius substantially larger than the indentation depth, thus restricting deformation to viscoelastic (and not plastic) modes in glassy polymers and permitting large loads and contact stiffness to be generated in compliant elastomers. Elastic-viscoelastic correspondence is used to generate spherical indenter solutions for a number of indentation testing protocols including creep following loading at a constant rate and a multiple ramp-and-hold protocol to measure creep response at several loads (and depths) within the same test. The finite ramp+creep solution is recast as a modification to a step-load+creep solution with a finite loading rate correction factor that is a nondimensional function of the ratio of experimental ramp time to the material time constant. Creep tests are performed with different loading rates and different peak load levels on glassy and rubbery polymeric materials. Experimental data are fit to the spherical indentation solutions to obtain elastic modulus and time-constant, and good agreement is found between the results and known modulus values. Emphasis is given to the use of multiple experiments (or multiple levels within a single experiment) to test the a priori assumption of linear viscoelastic material behavior used in the modeling.

4:45 PM R5.10
Nanomechanical Properties of TiO2/Epoxy Nanocomposites Using Instrumented Nanoindentation.
Stephanie Scierka, Peter L. Drzal, Amanda L. Forster and Stephanie Svetlik; Building and Fire Research Lab, NIST, Gaithersburg, Maryland.

Inorganic fillers, such as Titanium Dioxide (TiO2), have historically been added to polymeric coatings to enhance both the appearance properties and the mechanical durability. A common misconception is that these fillers are considered to be inert despite their semi-conductor electronic structure. Little regard has been given to understanding the accelerated polymer degradation that can result due to the nanoparticle photocatalytic activity when exposed to ultraviolet (UV) irradiation. Recent advances in instrumented nanoindentation offer the capability to characterize the dynamic mechanical and transient mechanical properties over much smaller length scales than can be measured through conventional rheological techniques. Model nanocomposite coatings consisting of a well-controlled, nanometer sized titanium dioxide particle filled systems were prepared. Three types of TiO2 particles were used in the production of the nanocomposite coatings. They differ in diameter from 50 nm to 300 nm and vary in UV reactivity due to surface treatment. A model epoxy system was chosen to provide a range of viscoelastic and UV degradation responses capable of being measured with nanoindentation. Each of the model nanocomposite coatings have been thoroughly mixed using a commercial dispersion apparatus. Pigment volume concentrations (PVC) up to 10%, the typical industry standard, have been used. Nanoindentation experiments were conducted measuring the change in viscoelasticity (dynamic and transient experiments) and indentation modulus with increasing volume fraction of pigment, particle size, and UV exposure. The measured changes in nanomechanical properties are evaluated in the context of bulk rheological (DMA), thermal (DSC), and chemical (ATR) measurements.

SESSION R6: Measuring Time Dependent Mechanical Properties with Point Probes

PANEL DISCUSSION
Tuesday, November 30, 2004
Room 202 (Hynes)
8:00 PM - 10:00 PM

Chairs: Nancy Burnham, Trevor Page, George Pharr, Mark Van Landingham and Kathryn Wahl

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SESSION R7: Nanotribology
Chairs: Yang-Tse Cheng and Judith Harrison
Wednesday Morning, December 1, 2004
Room 202 (Hynes)

8:00 AM *R7.1
Biomimetic Lubrication Schemes: Slippery When Wet.
Scott Perry[1], Xiaoping Yan[1], Nicholas D. Spencer[2], Markus Mueller[2] and Seunghwan Lee[2]; [1]Deparment of Chemistry, University of Houston, Houston, Texas; [2]Department of Materials, ETH-Zurich, Zurich, Switzerland.

The development of synthetic polymer lubricants to mimic joint lubrication within the human body will be presented. Unlike most industrial applications involving oils and greases, lubrication of these joints is accomplished in an aqueous environment. Fundamentally, water is a poor lubricant in most settings due to the weak pressure dependence of its viscosity, yet the contacting surfaces of skeletal joints function with low friction throughout a lifetime. Motivated by the molecular structure of materials making up joint surfaces, interfacial friction between polymer brush surfaces under aqueous environments has been probed with an array of molecularly sensitive surface analytical techniques including atomic force microscopy. The brush surfaces, comprised of poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG), have been generated through the spontaneous adsorption of polymer from solution onto oxide substrates and sodium borosilicate surfaces (AFM tip). The character of the polymer films has been investigated in-situ with the quartz crystal microbalance (QCM) and atomic force microscope (AFM) and ex-situ with ellipsometry and X-ray photoelectron spectroscopy (XPS). The interfacial friction measurements have been carried out on polymer-coated substrates with bare or polymer-coated, microsphere-attached tips in over a range of solution conditions. It was found that the adsorption of polymer on oxides strikingly reduced the interfacial friction, resulting in ultra-low friction under certain conditions. By using a series of PLL-g-PEG polymers differing from each other in PEG side-chain length and grafting ratio, we observed that frictional properties of polymer-coated interfaces strongly depend on the architecture of PLL-g-PEG. Polymer-film formation and the influence of polymer architecture will be reviewed while the role of solvent and manifestation of ultra-low friction will be discussed in detail.

8:30 AM R7.2
Fourier-Analyzed Shear Modulation Microscopy as a Probe of Molecular Mobility in Ultrathin Polymer Layers.
Greg Haugstad and Wayne Gladfelter; University of Minnesota, Minneapolis, Minnesota.

AFM-based shear modulation, plus Fourier analysis of time-domain response, has been used to explore the transition from static to sliding friction on ultrathin films of polyvinyl alcohol (PVA) on mica. The methodology exploits the third harmonic of response as a gauge of nonlinearity due to sliding. In the process, insight is obtained into the dramatic contrast seen in sliding friction images, in particular between a strongly adsorbed first layer and an autophobically dewetted second layer with bulk-like characteristics. The normal and shear stiffnesses of these layers (static friction regime) are found to be similar, whereas the transition to sliding takes place at significantly different drive amplitudes (approx. 1:2 in relative magnitude). This difference results in markedly different sliding friction forces (observed over many decades of scan velocity). Thus dissipative molecular motions are mobilized to a much higher degree on the second layer. Sliding friction on this layer under repeated scanning at high load further exhibits a history dependence that is interpreted via a two-state activation model, with activation energy on the order of a beta process. Together these findings indicate that bond rotations are arrested in the first layer but activated in the second layer via large tribological shear stresses. The importance of shear stress is corroborated by the relatively meager contrast seen in the energy dissipation during normal compression, tension and/or rupture of contact (other imaging modes, also spanning a wide range of measurement rates).

8:45 AM R7.3
Rough Surface Plasticity and Adhesion at Nanoscale.
Yanfei Gao and Allan F. Bower; Division of Engineering, Brown University, Providence, Rhode Island.

With the development of new nanomechanics models and new nanotechnologies, the study of mechanical and physical behaviors of interacting rough surfaces has been playing a central role in a broad spectrum of nanoscale research activities, including nanostructure fabrication and reliability, soft material adhesion, nanostructured coating design, nanotribology, among many others. The surface roughness typically has a multiscale nature, i.e. the existence of roughness details at many length scales. Material behavior becomes structure sensitive at mesoscale and nanoscale. Other than mechanical stresses and surface forces, the solid-solid interaction also involves physical forces from less familiar origins, such as surface stress, which are pronounced when the feature size is reduced. The above three aspects and their interactions contribute to the complex phenomena at mesoscale and nanoscale. In this work, we present a contact mechanics model based on the power spectral density function of the surface roughness. Using phenomenological strain gradient plasticity theory, we discover that one can only flatten asperities in a certain frequency interval of the roughness spectrum. We also present a new scheme of modeling rough surface adhesion by using the Dugdale model and self-affine fractal surface, which leads to a mechanism-based and history-dependent cohesive zone law. This work gives a scale-bridging mechanism study of mesoscale rough surface mechanics.

9:00 AM *R7.4
Contact and Friction between Rough Surfaces at the Nanometer Scale.
Mark O. Robbins[1,2], Binquan Luan[1], Sangil Hyun[1], Judith A. Harrison[3] and Noam Bernstein[4]; [1]Physics and Astronomy, Johns Hopkins Univ., Baltimore, Maryland; [2]Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland; [3]Chemistry, US Naval Academy, Annapolis, Maryland; [4]Naval Research Laboratory, Washington, District of Columbia.

Traditional theories of contact and friction are based on continuum models that break down at the atomic scale. Multiscale modeling techniques allow both atomic interactions at surfaces and larger scale elastic deformations to be treated realistically. We first present results for model single asperity contacts and compare them to Hertz and Johnson-Kendall-Roberts theories. Adding molecular scale roughness to a smoothly curving tip leads to dramatic changes in the contact size, pressure distribution and sub-surface stress field. We show that this makes it difficult to infer elastic and interfacial properties from experimental measurements of friction or conduction. The second part of the talk examines self-affine surfaces that have roughness on all length scales. Contacts between two and three dimensional surfaces are examined as a function of system size, roughness amplitude, roughness exponent and interfacial interactions. The scaling of contact area with load, the contact morphology and the pressure distribution are compared to finite-element calculations.

10:00 AM *R7.5
Nano-Science Via Nano-Spectroscopy.
Steve Granick, Jeffrey Turner, Sung Chul Bae, Ashis Mukhopadhyay and Zhiqun Lin; Materials Science and Engineering, Chemistry, and Physics, Univ. of Illinois, Urbana, Illinois.

There is growing awareness that the interpretation of nanotriboloy and other careful force measurements at the molecular and atomistic levels will benefit from ancillary local probes such as those obtainable by in-situ spectroscopic and scattering measurements of the interface. This laboratory has devoted considerable effort to combining force measurements (between mica sheets in the surface forces apparatus) with real-time measurements using not only vibrational spectroscopy, especially Raman and surface-enhanced Raman, but also few-molecule fluorescence spectroscopy, especially fluorescence correlation spectroscopy and time-correlated single-photon counting. An integrated picture emerges in which prior interpetations based solely on force measurements require some aspects of major modification based on information from these ancillary local probes. Time permitting, it will also be demonstrated that tribological processing of molecularly-thin conjugated polymers can also be employed to achieve novel photoluminiscent properties.

10:30 AM R7.6
Nanoscale mechanical studies of interfacial films from sliding contacts.
Gun Y. Lee, Irwin L. Singer and Kathryn J. Wahl; Code 6176, Tribology Section, U.S. Naval Research Laboratory, Washington, District of Columbia.

Friction, wear and endurance of solid lubricated contacts are controlled by the chemistry and dynamics of the interfacial films formed during sliding. By contrast, very little is known about the mechanical properties of these interfacial films, and how those mechanical properties influence the tribology. The interfacial films formed are challenging to study as they are often thin (few to hundreds of nm thick) and inhomogeneous on the micron scale. In this paper, we present an approach combining optical profilometry, scanned probe microscopy and instrumented indentation to evaluate the mechanical properties of worn surfaces and interfacial films. This approach provides high spatial resolution thickness and indentation information for any given region of interest. Reciprocating sliding tests on model solid lubricant coatings, MoS2 and Ti-Mo-S (MoST), were performed against sapphire hemispheres in ambient ($45 \leq$ % R.H. ≤ 60) air at 1-4 mm/s sliding speed. Transfer film thicknesses on the sapphire counterbody and on wear tracks was determined by optical profilometry and confirmed by scanned probe microscopy. The areas for mechanical analysis were selected based on thickness information and optical micrographs of the transfer film. Mechanical properties of the as deposited coatings, wear track surfaces, and counterbody transfer films were measured using a hybrid scanning nanoindenter in both point-analyses and stiffness imaging modes. The Ti-Mo-S coatings formed thicker transfer films (on average around 500 nm thick) than the MoS2 coatings. In both the MoS2 and Ti-Mo-S coatings, the hardness of transfer films formed was lower (50 % in MoS2 and 60-70% in Ti-Mo-S) than that of the coating. Transfer films on the wear track of the Ti-Mo-S coating showed low hardness values similar to the transfer film on the sapphire counterbody, while MoS2 wear track surfaces showed no measurable change in hardness. Most interestingly, the relative hardness of the transfer films compared to the unworn coatings was not a good indicator of the wear resistance of the coatings as might have been expected. We will discuss the challenges in quantifying measurements on these inhomogeneous thin films and interpreting the relationship between mechanical properties and tribological performance of MoS2 based solid lubricants.

10:45 AM R7.7
Nanotribology of High Quality Diamond-Like Carbon Films: Hydrogen-Free Tetrahedral Amorphous Carbon from Pulsed Laser Deposition, and Hydrogenated Diamond-Like Carbon from Plasma Immersion Ion Implantation and Deposition.
David Scott Grierson[1], A.V. Sumant[1], K. Sridharan[1], Erin E. Flater[1], J. P. Sullivan[2], T.A. Friedmann[2] and R.W. Carpick[1]; [1]Engineering Physics, UW-Madison, Madison, Wisconsin; [2]Sandia National Laboratory, Albuquerque, New Mexico.

High performance carbon films are of interest as coating materials for applications ranging from advanced tools and engine parts to micro- and nano-scale machines, where friction and wear must be exquisitely controlled. We have investigated the nanotribological properties (friction, adhesion, and wear) of two types of diamond-like carbon (DLC) films. One film, known commonly as tetrahedral amorphous carbon (ta-C), is grown with a Pulsed Laser Deposition (PLD) technique. It is essentially hydrogen-free and contains a high (up to 80%) fraction of sp3-bonded carbon. The other film is grown with the Plasma Immersion Ion Implantation and Deposition (PIIID) technique which is a unique non-line-of-sight method. This film is a hydrogenated DLC with a lower fraction of sp3-bonded carbon (30-50%). The surface chemistry and near-surface carbon hybridization are characterized via X-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy respectively. Our results confirm the distinct carbon bonding configurations in each of these films in the near-surface region. Atomic force microscopy (AFM) is used to quantitatively study the nanotribological properties of these films for the first time by measuring single asperity friction and adhesion using both silicon nitride AFM tips and AFM tips coated with DLC and ta-C. We find that these films exhibit low overall friction and adhesion but are sensitive to the relative humidity. We will discuss the connection between film structure and nanotribology as revealed by these measurements. 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.

11:00 AM R7.8
Small Volume Tribological Testing of LIGA Nickel.
Neville R. Moody[1], John M. Jungk[2], Marion S. Kennedy[3], Soumari V. Prasad[4], David F. Bahr[3] and William W. Gerberich[2]; [1]Sandia National Laboratories, Livermore, California; [2]University of Minnesota, Minneapolis, Minnesota; [3]Washington State University, Pullman, Washington; [4]Sandia National Laboratories, Albuquerque, New Mexico.

Strength, friction, and wear are dominant factors in the performance and reliability of materials and devices fabricated using nickel based LIGA and silicon based MEMS technologies. However, the effects of frictional contacts and wear on long-term performance of microdevices are not well-defined. To address these effects on performance of LIGA nickel, we have begun a program employing nanoscratch and nanoindentation. Nanoscratch techniques were used to generate wear

patterns using loads of 100, 200, 500, and 990 mN with each load applied for 1, 2, 5, and 10 passes. Nanoindentation was then used to measure properties in each wear pattern correcting for surface roughness. The results show a systematic increase in hardness with applied load and number of nanoscratch passes. In this presentation, we will use measured hardness values and Johnsons cavity model for plasticity to show how flow stress and the extent of plasticity evolve under sliding contacts. We will also show that the work hardening coefficient determined from indentation tests within the wear patterns follows the results established from tensile tests, supporting use of a nanomechanics-based approach for studying wear. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

11:15 AM R7.9
Work of Adhesion Between AFM Cantilever Tips and Unpatterned Silicon Die. Erik Thoreson[1], J. Martin[2] and N. A. Burnham[1]; [1]Physics, Worcester Polytechnic Insitute, Worcester, Massachusetts; [2]Analog Devices, Inc., Cambridge, Massachusetts.

If moving micro- or nanostructures touch, recovery requires that restoring forces overcome the surface adhesive forces. To study restoring forces, we have calibrated cantilever probes for an Autoprobe M5 AFM from Veeco, so that the work of adhesion can be determined to an accuracy of about 20% [1,2]. Hence, we will present our results for the calibrated works of adhesion between AFM tips (60 μm, 6 μm, 2 μm, and less than 1 μm radius tip) and unpatterned silicon die that were solder-sealed in 5 mm x 5 mm LCC (Leadless Ceramic Chip Carrier) packages. Two sample variables were examined; four die attach conditions (no attachment, silicone, polyimide silicone, and silver glass) and two surface conditions (with and without a few angstroms of vapor-deposited diphenyl siloxane). All measurements were made at a relative humidity of 24.5 $\pm$ 1.5 % and a temperature of 22.5 $\pm$ 1.9 °C. DMT (Derjaguin, Muller, and Toporov) contact mechanics was employed to calculate the works of adhesion on all samples from the measured adhesive force and radius of the cantilever tip. Data for the 60 μm radius cantilever tip indicate that the treated surfaces had a lower work of adhesion as compared to the untreated counterparts; the untreated silicone and silver glass die-attachments had the highest work of adhesion, and the surface-tip interface may have been dominated by material transfer. A cleaning procedure for the cantilever was developed that seemed to reduce the work of adhesion for the 60 μm tip radius but was less effective for smaller radii. Future work will include developing a set of specifications for an in-fab stiction monitor. 1. N A Burnham, X Chen, C S Hodges et al., Nanotechnology **14**(1), 1-6 (2003). 2. E. J. Thoreson and N. A. Burnham, Review of Scientific Instruments **75** (5), 1359-1362 (2004).

MRS MEDAL AWARD TALK PRESENTATION

11:30 AM *R7.10
Importance of the Sub-$\mathring{a}$ngstrom (pico-scale) Topography of Surfaces for Adhesion, Friction and Different Modes of Failure. Jacob Israelachvili, Department of Chemical and Nuclear Engineering, University of California-Santa Barbara, Santa Barbara, California.

The talk will review some recent experimental results, including theoretical modeling and computer simulations, on the effects of surface texture, surface energy and the bulk properties of materials on their adhesion and friction and, in turn, on some of the fundamental differences between Mode I and Mode II failure of materials. Examples and comparisons will include surfaces that are rough or smooth, hard or soft (e.g., viscoelastic), adhesive or non-adhesive, dry (unlubricated) or lubricated. Such studies are clarifying the molecular and atomic basis of many well-established adhesion and tribological laws and empirical observations, and revealing new insights and relationships between nano-scale (molecular) and macro-scale processes. The talk will focus on the sometimes crucial importance of effects that occur at the sub nano-scale, i.e., in the sub ngstrom or pico-scale regime. It will be shown and argued that the ultra-fine pico-scale details of a surface lattice or its roughness can be the most important factor in determining its friction and Mode II fracture, whereas such effects are quantitatively less important for adhesion and Mode I fracture processes.

SESSION R8: Nanomechanics and Tribology of Thin Films
Chairs: Norbert Huber and Mark Robbins
Wednesday Afternoon, December 1, 2004
Room 202 (Hynes)

1:30 PM *R8.1
Atomic-Scale Tribology of Solid Lubricants. Judith Harrison[1], Paul T. Mikulski[2], Guantu Gao[1] and Ginger M. Chateauneuf[1]; [1]Chemistry, US Naval Academy, Annapolis, Maryland; [2]Physics Department, US Naval Academy, Annapolis, Maryland.

The rapid development of MEMs as prompted the need for protection of the surfaces of these devices. Amorphous carbon films (a-C and a-CH) and self-assembled monolayers (SAMs) are both possible candidates for the passivation and lubrication of MEMs. The fundamental problem associated with controlling friction and wear is a lack of understanding of the underlying atomic-scale chemical and physical processes that govern them. We have done extensive molecular dynamics (MD) simulations that have examined the compression and friction of model hydrocarbon SAMs attached to diamond and amorphous carbon films attached to diamond. We have examined the contact forces present at the interface between a tip and pure, or mixed-length, SAMs during sliding. The contact forces lend insight into the difference in observed friction of pure and mixed-length SAMs. Compression and shear-induced polymerization have also been modeled in unsaturated hydrocarbon films. In addition, we have also done extensive simulations that analyze the structure and friction of a-C and a-CH films. Some of our recent results will be discussed.

2:00 PM R8.2
Mechanical and Tribological Testing of Nanolaminated Carbon Based Films for Protection of Optical Systems. Spyros Kassavetis, Panos Athanasios Patsalas and Stergios Logothetidis; Physics, Aristotle University, Thessaloniki, -, Greece.

Amorphous Carbon (a-C) and hydrogenated a-C (a-C:H) films have been established as very important engineering materials with exceptional mechanical properties. Especially the hard tetrahedral (sp3) a-C films are successful as protective overcoats, e.g. on magnetic disks. One of the inherent limitations in the growth of stable and sustainable hard a-C is the development of high compressive stress, which is thickness-dependent and may cause delamination and failure. A solution to this problem has been proposed to be the growth of a-C nanolaminates with alternating a-C layers (few nm thick) rich in sp2 and sp3 hybridized carbon [1,2]. In this work, we grow from the vapour phase and mechanically test a wide variety of a-C and more transparent a-C:H nanolaminates (with individual layers 5-10 nm thick), as well as their constituents i.e. thin monolithic a-C and a-C:H films. The morphology and hybridization of the films are studied by X-Ray Reflectivity, Atomic Force Microscopy (AFM) and X-Ray Photoelectron Spectroscopy. Acoustic AFM in cross-section geometry is also used to investigate the variations of the elastic behaviour of the individual layers. We investigate the appropriate alteration and composition of the various a-C/a-C:H layers, which provide a combination of excellent mechanical and tribological behaviour and high optical transparency (evaluated by in-situ spectroscopic ellipsometry), in order to be used for protection of optical devices such as lenses and photovoltaics. The continuous stiffness measurements technique was used to measure hardness (H) and elastic modulus (E), as a function of depth. The Bhattacharya-Nix equation, for the substrate effect on the measured H, was applied in order to extract the film's real hardness (Hf). Large deviations between Hf and H were found in hard multilayers. Hf, being up to 36 GPa, has been found to be strongly correlated with the sp3 and hydrogen contents and the bilayer thickness. The nanotribolgical behaviour of a-C/a-C:H is also investigated using lateral force measurements. Low load scratch tests were used to evaluate the scratch resistance and the friction coefficient of the nanolaminates. The scratch process revealed a fully elastic recovery/deformation of the coatings. Testing under a normal load of 6 mN resulted in slight grooving at the layer surface; however, in-situ profiling of the scratch trace showed no evidence of failure. The values of friction coefficient were found in the range of 0.1-0.3 depending on the sp3 and hydrogen contents. [1] M. Gioti, S. Logothetidis, C. Charitidis, Appl. Phys. Lett. 73, 184 (1998). [2] C. Mathioudakis, P.C. Kelires, Y. Panayiotatos, P. Patsalas, S. Logothetidis, Phys. Rev. B65, 205203 (2002).

2:15 PM R8.3
Nano Scratching of Clear Coats and Relation to Mechanical Material Properties. Claus D. Eisenbach[1,2], Rolf Nothhelfer-Richter[1] and Marco Kordisch[1]; [1]Research Institute for Pigments and Coatings, Stuttgart, Germany; [2]Institute of Applied Macromolecular Chemistry, University of Stuttgart, Stuttgart, Germany.

The nano single scratch experiment has been proven to be a suitable method to evaluate the scratch resistance of a coating. The single scratch damage and its recovery have been studied for a variety of clear coats under dry as well as wet conditions; these investigations were complemented by multi-scratch tests. The bulk mechanical materials properties of free standing films of the clear coats were determined by tensile tests and dynamic mechanical analysis (DMA). Among other things it was found that the recovery of the scratch groove is inversely related to the maximum value of the loss tangent

(tan d) as obtained from DMA analysis. The results of our comparative experiments and implications for the evaluation of the scratch resistance of organic coatings will be discussed.

2:30 PM *R8.4
Molecular rearrangements and conformational transitions under confinement. Manfred P. Heuberger, Materials, Swiss Federal Institute of Technology, ETH, Zurich, ZH, Switzerland.

Using the extended surface forces apparatus we are probing molecular re-arrangements and conformational transitions - in some cases at sub-Angstrom resolution. The phenomenon of stick-slip is revisited in the case of a simple linear alkane system, which acts as model lubricant. Film-thickness changes are monitored during intermittent slip events and the film relaxation during stop-start experiments is recorded. The effects of molecular ordering and the presence of nano-particles on the dynamics of friction are discussed. A water-soluble, PEG containing co-polymer architecture is used to construct a water-based lubrication system. A high-resolution measurement of the compression isotherm reveals film-thickness transitions under confinement that are due to a water-induced restriction of the conformational space of PEG. These findings are in accord with known solution properties of this polymer. The friction is found to be vanishing small in a dilute aqueous solution of this co-polymer.

3:30 PM R8.5
In Vivo Nanostructural Origin of Metal-on-Metal Hip Joint Wear Particles. Alfons Fischer[1], Robin Buescher[1], Georg Taeger[2] and Markus Wimmer[3]; [1]Mater. Sci. Eng. II, University of Duisburg-Essen, Duisburg, Germany; [2]Trauma Surgery, University of Duisburg-Essen, Essen, Germany; [3]Orthopedics, Rush University Medical Center, Chicago, Illinois.

The second generation of all-metal hip joints increasingly gains acceptance since they are known to generate substantially fewer wear than metal-polyethylene and ceramic-polyethylene couples. However, with an average size of far below one micron up to 1014 particles are released from a metal-on-metal (MOM) articulation each year and migrate into the surrounding tissue. Thus, the generation of wear particles is still a major cause of concern. In parallel the acting mechanisms, which hinder the formation of such particles, are of interest, because they might lead to life times exceeding the nominal 10 years by far. Thus, 42 retrieved McKee-Farrar prostheses made out of CoCr29Mo6 alloy with a complete clinical record were investigated as to the acting wear mechanisms. By means of a combined approach in identifying the wear mechanisms on and under the contacting surface in vivo substantial new information has been gained by the authors. At first they can show, how the particles are formed by mechanically dominated wear mechanisms under the contact area. Within a nanocrystalline layer of about 200 to 500 nm thickness surface fatigue prevails on a nm-scale and brings about globular metallic particles with a size below 100 nm. At the same time a strain induced phase transformation below that layer leads to needle shape martensite. This fractures close to the surfaces, because of the strain gradient brought about by the friction forces, and generates metallic needle or lamellar shape particles of the same length. Both are that small that they act more as a solid lubricant than as abrasive particles. Nevertheless, bigger agglomerates of both might act as loose particles inside the gap between ball and cup. Further it was found in vivo that beside anorganic Cr- and O-rich layers of 30 nm thickness in addition organic C-rich patches of 100 nm thickness cover a large fraction of the contact areas of such hip joints. Both are generated by tribochemical reactions of the contacting surfaces with the interfacial medium. The Cr-O-layers are nothing but passive layers of Cr2O3 type. By means of protein standards the organic origin of the C-rich patches could be verified. Since especially these are 100 nm thick and adhere rigidly to the Cr2O3 ones they bring about the real area of solid contact in this mixed lubrication regime. They take a certain fraction of the contact, hinder any direct metal-to-metal contact. Nevertheless, these layers and patches wear off the surfaces, which can understood as the basic mechanism of tribochemical reactions by the generation and delamination of the tribochemical reaction layers. Thus, in addition to the metallic particles oxidic ones of similar size have been found.

3:45 PM R8.6
Nanoindentation of silicon nitride, silicon oxide, and germanium thin films. Mariusz Martyniuk, J. Antoszewski, B.A. Walmsley, H. Huang, C.A. Musca, J.M. Dell and L. Faraone; School of Electrical, Electronic and Computer Engineering, The University of Western Australia, Crawley, Western Australia, Australia.

Material properties of thermally evaporated germanium, as well as plasma enhanced chemical vapour deposited (PECVD) silicon nitride and silicon oxide thin films have been investigated using nanoindentation experiments. Thin films spanning a thickness range of 0.1-1.1μm were deposited on silicon substrates and nanoindentations were performed in a penetration depth range of 0.03-2.5μm. The elastic modulus, E and hardness, H values of all examined film/substrate bilayers were found to vary asymptotically from the thin film properties (E_{Ge} = 108GPa, H_{Ge} = 4.4GPa, E_{SiO} = 67GPa, H_{SiO} = 6.2GPa) for shallow indents to the substrate properties (E_{Si} = 168GPa, H_{Si} = 12.6GPa) for deep indents. A simple empirical formulation is shown to relate E and H of the film/substrate bilayer to corresponding material properties of the constituent materials via a power-law relation. The material properties of PECVD silicon nitride were found to be dependent on the deposition temperature, and both E and H followed similar trends. Constant E and H (E_{SiN} = 157GPa, H_{SiN} = 14.8GPa) were observed for deposition temperatures above 200°C. Decreasing the deposition temperature was found to initially cause a gradual decrease in the E and H parameters, followed by an abrupt decrease in E and H once the deposition temperature is lowered below 100°C (E_{SiN} = 50GPa, H_{SiN} = 3.6GPa at a deposition temperature of 50°C).

4:00 PM R8.7
Indentation Size Dependence of Apparent Elastic Modulus in Nano-grained Ni-25at.%Al Alloy Film. Han Li and A.H.W Ngan; Mechanical Engineering, the University of Hong Kong, Hong Kong, Hong Kong.

The design, fabrication and reliable operation of miniaturized devices and systems require knowledge of material properties down to the nanometer length scale. In this paper, we present a cyclic indentation investigation of elastic modulus as a function of the indentation peak load or indent size on three kinds of samples: fused quartz, single crystal Ni_3Al (111) and nanocrystalline Ni-25at.%Al alloy thin film with average grain size of a few nm. The load ranges from 50μN to 10 mN. Indentation hardness, apparent Young's modulus and incipient plasticity, if any, were measured. Interestingly, a size dependence of the elastic modulus was only observed in the thin film sample with the modulus value decreases at smaller indent depths, and the scattering of indentation response becomes more drastic. AFM imaging reveals that the observed size effect of Young's modulus originates from the peculiar microstructure of the thin film. Three representative scenarios were identified at very small indentation depths which can explain the size effect of the apparent hardness and modulus and the overall trend of their scatter: (I) intra-columnar indentation, showing an almost reversible contact within experimental error, (II) intra-columnar indentation, in which the column is pressed downwards, and (III) inter-columnar indentation, in which neighboring columns are plastically pushed apart. Other situations can be regarded as a combination of these three. Elastic contact is observed only in scenario I, while in the other two scenarios, the deformation is elastoplastic from the very beginning leading to significantly lower hardness and modulus values. Repeated indentations in scenario II show a compaction-like effect and produce indentation responses approaching that in scenario I, which results in an effective Young's modulus close to the bulk value. In all cases, pop-in is rarely observed. As for hardness, the fused quartz shows an almost constant value at all depths while the Ni_3Al single crystal and the nanocrystalline alloy film both exhibit a significant size effect. The increase of hardness in the nanocrystalline alloy from relatively large depths to intermediate depths can be understood by considering mainly the surface energy change. At even smaller depths, the location dependent deformation mechanisms greatly increase the scatter of the hardness value and result in an overall decreasing trend.

4:15 PM R8.8
Effect of Thin Films on the Strength of Silicon in the Region of Small-Scale Flaws. Yeon-Gil Jung, Antonia Pajares and Brian R. Lawn; Materials Science and Engineering Laboratory, NIST, Gaithersburg, Maryland.

Silicon remains the principal material component of MEMS and NEMS devices. Such materials can be fabricated in near-defect-free form with strengths well in excess of 1 GPa. However, real devices are subject to submicroscopic damage under long-term operating conditions, most notably from small-scale contacts. Among many important issues is the retention of strength during the lifetime of the device as small-scale flaws evolve in the structures. In particular, how is strength influenced by the presence of thin films on the silicon surface? The present study uses nanoindentation to introduce controlled flaws of ever-decreasing size into silicon plates with dense thermally grown oxide and LPCVD nitride surface films. Strength tests are conducted by bonding the indented plate surfaces to a polycarbonate substrate, and then applying a concentrated axial load at the top surfaces to induce fracture from the indentation sites. The measured strengths for pristine silicon sytematically increase with decreasing flaw size, the increase becoming more rapid below an indentation threshold at which well-developed indentation pre-cracks become suppressed. The strengths for silicon with oxide films are greater over the entire indentation load range, but especially in the

subthreshold region. Conversely, the strengths for silicon with nitride films are degraded over the load range. These trends are consistent with the existence of compressive stresses in the oxide and tensile stresses in the nitride. A simple fracture analysis is used to quantify the residual stress levels.

4:30 PM R8.9
Development of In-Situ, Small-Scale Mechanical Testing Protocols for Microsystem Packaging. Marvin Francis, Satyajit Walwadkar and Junghyun Cho; Mechanical Engineering, SUNY Binghamton, Binghamton, New York.

There is a growing demand in the development of small-scale devices in microelectronics and microelectromechanical system (MEMS) applications. Packaging and reliability of such devices are of great concern, since they introduce a number of unique packaging issues that are distinct and different from typical electronic packaging applications. In addition, the packaging or encapsulation materials are often exposed to harsh environments such as elevated temperatures, corrosive media, and moisture absorption, for which their mechanical performance is not well known. Recent developments of a depth sensing indentation (nanoindentation) and atomic force microscope (AFM) are powerful instruments that permit the observation and characterization of various packaging materials at such small scales. These instruments are particularly useful for localized, small-volume structures and thin films whose behavior is not easily predicted from bulk properties. Furthermore, with an add-on dynamic loading capability, polymeric materials that often exhibit a strong time-dependent deformation can be well characterized. Packaging is by nature a multilayer, multicomponent system, where materials properties are constrained by adjacent structures, thus making the nanoindentation more suitable in this application. The testing under ambient conditions no longer provides accurate data for the materials if the devices are to be exposed to harsh environments. In-situ mechanical testing under a condition that emulates specific environment will thus be beneficial for evaluation of packaging materials. Given that, we specifically focus on: i) development of nanoindentation testing for polymeric materials used in microsystem packaging; ii) time-dependent deformation (viscoelasticity) of polymers via continuous measurement of contact stiffness; iii) parallel study with conventional tensile/bending tests to corroborate the nanoindentation data.

4:45 PM R8.10
Characterization of Nanoindentation-Induced Failure by Monitoring Acoustic Emission. Pawel Dyjak and Raman P. Singh; Department of Mechanical Engineering, Stony Brook University, Stony Brook, New York.

When a brittle material is loaded by a sharp indenter, radial cracks propagate out of the indenter corners if a sufficiently large load is applied. The measured lengths of these cracks can then be used to estimate the effective fracture toughness of the brittle material. While this procedure is adequate for providing an averaged measure of fracture toughness in homogeneous materials, it provides no information regarding the progression of crack initiation and growth. Furthermore, this technique cannot delineate energy dissipation by various fracture processes that might occur for a locally heterogeneous material. In this investigation we employ the monitoring of acoustic emission (AE) activity during nanoindentation-induced failure to characterize the initiation and progression of local fracture processes. Specimens of various brittle materials were loaded with a cube-corner indenter in a NanoTest instrument (Micro Materials Ltd., Wrexham, United Kingdom). Acoustic emission activity was monitored the entire loading and unloading event using an AE transducer (Vallen-Systeme GmbH, Munich, Germany) mounted inside the specimen holder. By locating the AE sensor directly underneath the sample it was possible to eliminate spurious signals that may occur when the diamond indenter is not effectively in contact with the sample. Acoustic emission signals were recorded and correlated with the nanoindentation data in real time, using the following parameters: threshold value of 21.9dB, sensor response range between 100 to 400 kHz, transient sampling rate of 10 MHz and parametric timing of 0.001s. Experiments were carried out at various loads including 25 mN, 125 mN, 225 mN, 250 mN and 450 mN for both single loading, and multiple loading-unloading conditions. The four materials tested include soda lime glass, a glass-ceramic, Macor (Corning Inc., Corning, New York), beta crystalline silicon carbide (Rohm and Haas Co., Woburn, Massachusetts) and amorphous silicon carbide. As observed from the nanoindentation and acoustic emission response, there were fundamental differences in the fracture behavior of these materials. Post-failure observations were used to identify particular features in the AE signal (amplitude, frequency, rise-time) that correspond to specific types of fracture events. Furthermore, analysis of the parametric and transient AE data was used to establish the crack-initiation threshold, crack-arrest threshold, and energy dissipation during fracture. It was demonstrated that the monitoring of AE signals yields both qualitative and quantitative information regarding highly local failure events in brittle materials.

SESSION R9: Poster Session: Nanoindentation and Nanotribology
Chairs: David Bahr, Yang T. Chang, Norbert Huber, Adrian Mann and Kathryn Wahl
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

R9.1
Nanoindentation Studies on Polyelectrolyte Multilayers and Polyelectrolyte-based Nanocomposite Films. Adam J. Nolte[1], Robert E. Cohen[2] and Michael F. Rubner[1]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The modulus and hardness of polyelectrolyte multilayer (PEM) films and PEM composite films with nano-sized filler materials have been investigated by nanoindentation. Thin films assembled from poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) solutions allow one to tailor the degree of ionic cross-linking and the specific chemical functionality available within the assembled film by varying the pH of the deposition solutions. PAH/PAA multilayers can become templates for the creation of nanocomposite materials by exploiting the internal chemical properties of the film. For example, films assembled at certain pH conditions have a large number of free carboxylic acid groups from the PAA chains that facilitate post-assembly nanoreactor chemistry to introduce various nanoparticle species into the film. Also, post-assembly porosity transitions introduce size-tunable pores that can be filled with various materials through infiltration-reaction schemes. In this study, we examine the effect of varying degrees of cross-linking on the mechanical properties of PEM films, as well as the mechanical advantages involved in incorporating different loading amounts of silver nanoparticles and other nano-sized fillers within the polyelectrolyte matrix. We also discuss methods to control the spatial distribution of composite materials within PEMs, and the advantages of such techniques for improving mechanical properties such as the wear resistance of the film.

R9.2
Aspects of Tip Shape Characterization for Nanoindentation of Compliant Materials. Mark R. VanLandingham, Materials Division, U. S. Army Research Laboratory, Aberdeen Proving Ground, Maryland.

The application of nanoindentation methods to compliant materials, such as polymeric and biological materials, often requires the use of instrumentation designed with enhanced low-force sensitivity. Achieving such low-force sensitivity generally limits the maximum force level that the system is capable of applying. Because tip geometry is normally characterized using indentation of a relatively stiff reference material, such as fused silica, the maximum contact depths achieved by low-force instruments during this calibration are typically around 500 nm or less. However, penetration into compliant materials with modulus values that are several orders of magnitude lower than fused silica is often several micrometers or more. Depending on the particular tip geometry, extrapolation of tip shape data from fused silica indentation can lead to significant uncertainties in the indentation measurements for compliant materials. In this research, atomic force microscopy (AFM) methods are used to provide additional tip shape information, both in terms of characterizing a larger range of depth and also providing three-dimensional tip information. Comparative measurements are being performed using indentation of fused silica, scanning nanoindentation tips across "tip characterization" samples, and direct imaging of nanoindentation tips using AFM.

R9.3 TRANSFERRED TO R5.7

R9.4
Effects of Surface Stress on the Load-Depth Curves of Depth-Sening Indentation. Qing Wang and Koichi Ozaki; Digital Manufacturing Research Center, AIST, Tsukuba, Japan.

Residual stresses induced during mechanical process have either a beneficial or a detrimental effect and play an important role in structure service life. As a non-destructive method, a depth-sensing indentation system was used to measure the residual stress in the stainless steel. Different from other measurement methods, such as X-ray diffraction technique, depth-sensing indentation can provide an accurate measurement of residual stress with unknown material

properties. Effects of surface stress on the load versus depth curves of depth-sensing indentation are carefully investigated. These load versus depth behaviors represent a fingerprint of the surface stresses of the material investigated. Based on the investigation, a new experimental scheme for determination of the residual stress by indentation is suggested. The surface stress is correlated to the load shift induced with the surface stress using energy method.

R9.5
A Critical Examination of the Contact Area used in Analyzing Nanoindentation Data Based on 3D Finite Element Modeling. Sanghoon Shim[1] and G.M. Pharr[1,2]; [1]University of Tennessee, Knoxville, Tennessee; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Much of our understanding of the elastic-plastic contact mechanics needed to interpret nanoindentation data comes from two-dimensional, axisymmetric finite element simulation of conical indentation. In many instances, conical results adequately describe real experimental results obtained with a triangular pyramidal indenter like the Berkovich, particularly if the angle of the cone is chosen to give the same area-to-depth ratio as the pyramid. For example, conical finite element simulations with a cone angle of 70.3 deg. have been found to accurately simulate experimental load-displacement curves obtained with a Berkovich indenter. There are instances, however, where conical simulations fail to capture important behavior. Here, 3-D finite element simulations of Berkovich indentation of fused silica are compared to similar simulations with a 70.3 deg. cone to identify important differences. It is shown that a potentially significant difference exists between the contact areas at a given indentation depth. Implications for the interpretation of nanoindentation data are discussed.

R9.6 TRANSFERRED TO R1.8

R9.7
Spherical Load Indentation in Submicron NiTiCu Shape Memory Thin Films. R. Hassdorf[1], J. Feydt[1], S. Thienhaus[1], L. Buforn[2], N. Conte[2], O. Pykhteev[1], M. Kruzik[1,3], N. Botkin[1] and M. Moske[1]; [1]Research center caesar, Bonn, Germany; [2]CSM Instruments SA, Peseux, Switzerland; [3]Academy of Sciences, Prague, Czech Republic.

Nanoindentation with spherical tipped indenters provides a powerful technique to explore surface and thin film mechanical properties through the application of Hertzian contact mechanics. The full range of mechanical response can be obtained from elastic, through the yield point, to permanent deformation. So far, however, less is known in case of structural transformation or otherwise higher complexity of the material under investigation. As observed, e.g., in shape memory alloys, stress-induced martensitic transformation results in superelasticity. In this respect, we present a study on MBE-grown submicron NiTiCu alloy thin films using spherical load indentation. The indentation measurements were performed starting from the parent austenite state. Notably, for loads as small as 0.5 mN, deformation appears to be completely reversible. As loading is increased (up to 5 mN) the indent becomes irreversible following local plastic deformation within the tip-specimen contact area. Using an analytical approach the indentation data were converted into a stress-strain diagram aimed at simulating uniaxial tension load. Therefrom, the width of the superelastic region is estimated to be around 1-1.5% strain. This complies with finite-element simulations used to fit the indentation curves. Finally, comparison with uniaxial tension experiments will be made. Supported by BMBF under contract no. 03N4031A.

R9.8
Abstract Withdrawn

R9.9
Experimental and Numerical Analysis of the Interaction between Surface Roughness, Capillarity and Adhesion in MEMS. Frank W. DelRio[1,2], Maarten P. de Boer[1] and Martin L. Dunn[2]; [1]Reliability Physics Department, Sandia National Laboratories, Albuquerque, New Mexico; [2]Department of Mechanical Engineering, University of Colorado, Boulder, Colorado.

Interfacial adhesion and friction remain limiting factors in the reliability of MEMS devices. One important issue is that a thorough understanding of the interaction between surface roughness and capillarity is lacking. The structural material we study is polycrystalline silicon (polysilicon), which exhibits nanometer scale root mean scale (rms) roughness. Hard, carbonaceous contaminant particles (25-50 nm high) may also exist on the surface as a result of the release process. These surface features have been shown to affect adhesion on the local scale. In this paper, we conduct experimental and numerical analysis of the interaction between surface roughness, capillarity and adhesion in microcantilevers. Our experiments are performed in a state-of-the-art environmental interferometric chamber. The particle density is measured using tapping mode atomic force microscopy and is approximately twenty per μm^2. Oxygen plasma (800 V DC, 200 mTorr) has been shown to significantly reduce the particle density. Without plasma cleaning, microcantilever adhesion does not increase until 90% relative humidity (RH), while after plasma-cleaning adhesion begins to increase as low as 45% RH. Yet, different polysilicon roughnesses do not yet impact the adhesion versus RH trend. We will optimize the plasma conditions to further lower the particle density in an effort to observe the expected effect of polysilicon roughness in the adhesion versus RH trend. In our modeling approach, we apply finite element analysis to gain insight into the connection between surface roughness and adhesion. The intriguing open issues involve the interpretation of adhered microcantilevers in the context of a fracture mechanics framework. Namely, because the compressive pressure just in front of the crack tip required to support the applied moment of the adhered cantilever is 1000 times larger than the adhesive pressure due to van der Waals forces, and because the rough interface is more compliant than the bulk polysilicon, the surface separation will locally become smaller. This area, therefore, is likely to play a key role in the nucleation of capillaries. A complete understanding of the pressure distribution in front of the crack tip and of capillary bridging forces behind the crack tip is required. The crack tip mechanics in the presence of increasingly sophisticated representations of the actual physical situation will be modeled with the aim of developing a mechanistic understanding of the complex behavior often exhibited in adhesion measurements. These include the van der Waals force, rough interfaces as defined by contacting asperities, and the effects of bridging tractions as induced by humidity. Acknowledgement: 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.

R9.10
Initiation of Stick-Release via Dynamic Excitation. Amit Arvind Savkar[1], Kevin D. Murphy[1] and Mathew R. Begley[2]; [1]Division of Applied Mechanics Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269-3139, Connecticut; [2]Structural and Solid Mechanics Program Department of Civil Engineering, University of Virginia, Charlottesville, VA 22904-4742, Virginia.

The objective of the current work is to determine analytically whether dynamic excitation may be used to repair stiction-failed cantilevers. This is accomplished by relating the structural dynamic response to the de-cohesion of stiction-failed micro-cantilever beams under various loading conditions. Modal analysis is used to describe the dynamic response of the stiction failed micro-cantilever beams. Using dynamic fracture models in assistance with the modal analysis, a procedure to predict the onset of decohesion of the adhered cantilever beam is established. Specifically, decohesion is initiated when the dynamic energy release rate exceeds a critical interface fracture energy, which is known to control adhesion. Dynamic excitation parameters that promote debonding between the adhered portion of the beam and the substrate are presented. Point load, distributed load and patch load are considered for excitation of the beams. As expected, the dynamic force amplitudes needed to trigger debonding are significantly lower than the required static force, when the excitation frequency approaches the first natural frequency of the adhered beam. However, for higher excitation frequencies, dynamic effects can either promote or hinder debonding, depending on which vibration modes are induced. Such studies are presented for all three loading cases. Closed form, steady-state analytical solutions are presented as a conservative estimate of predicting the release of stiction failed beams along with a more rigorous implementation of a transient analysis. It has been established that the transients induced in the system often play a significant role in reducing the force required to initiate decohesion.

R9.11
Self-Organized Criticality in Nanotribology. Alan Schilowitz[1], Dalia Yablon[1] and Fredy Zypman[2]; [1]Corporate Strategic Research, Exxon Mobil Research and Engineering Co., Annandale, New Jersey; [2]Department of Physics, Yeshiva University, New York, New York.

We have already shown that dry sliding as measured by AFM lateral force satisfies the most important characteristics for self-organized criticality (SOC), that is that stick-slip jumps are distributed according to a power law. In order to further support the hypothesis that jumps in dry friction follows SOC we performed other tests. Most notably, we checked whether the frequency power spectrum follows a power law. In this paper we will report on the first such experiments done using an AFM to establish the presence of SOC in dry friction. The data, obtained with a nanotribometer - an Atomic Force Microscope set to measure lateral forces, examines the variation of the friction force as a function of time. We used surfaces of quartz, steel,

silica and mica. An analysis of the data shows that the probability distribution of slip sizes follows a power law. In addition, the frequency power spectrum follows a 1/fâ pattern with an exponent larger than unity. We performed an analysis of all the properties that are required to guarantee the presence of self-organized criticality. Our data strongly support the existence of self-organized criticality for nano-stick-slip in dry sliding friction. We also correlate the parameters of SOC with the surfaces under study and from the results propose a new method of materials characterization based on the slopes of SOC and power spectra. FZ acknowledges support of Research Corporation through grant CC5786.

R9.12

TEM Observation of Microstructural Change of Silicon Single Crystal Caused by Scratching Tests Using SPM.

Makoto Takagi[1], Kenji Onodera[2], Hiroyuki Iwata[3], Toru Imura[1], Katsuhiro Sasaki[4] and Hiroyasu Saka[4]; [1]Mechanical Engineering, Aichi Institute of Technology, Toyota, Japan; [2]Graduate School, Aichi Institute of Technology, Toyota, Japan; [3]Electrical and Electronics Engineering, Aichi Institute of Technology, Toyota, Japan; [4]Quantum Engineering, Nagoya University, Nagoya, Japan.

Nanotribology is one of the important factors for the practical use of NEMS or another engineering applications. In this study, the microstructural change of the surface of Si single crystal after the scratching tests under very small loading forces was investigated by cross-sectional TEM observation. Line-scratching tests and scanning-scratching tests using atomic force / friction force microscope (AFM/FFM) were carried out to investigate the nanotribological behavior of Si single crystal. In the both scratching tests, the loading forces of a diamond tip of AFM/FFM were changed over a range from 1μN to 200μN. The scratching direction of the tip was <110> on Si(100) surface, and the scratching velocity was 5μm/s. In the line-scratching tests, the scratching length was 10μm. In the scanning-scratching tests, the area of 5μm×5μm was worned by the scanning of 512 lines per cycle, and the number of the cycles was varied from 1 to 20. Cross-sectional TEM observations of the wear traces which were generated by the above-mentioned scratching tests were carried out. Focused-ion beam (FIB) was used to prepare the specimens for TEM observations. As a result of TEM observations after line-scratching tests, it was found that the depth and the width of the wear traces increased with increasing the loading force, and the shape of the wear traces was clearly replicated that of the diamond tip. In the case of the loading forces of more than 5μN, dislocation loops or small dislocations were observed in the area of less than 100nm thickness from the surface of the wear traces. In the case of the loading forces of more than 20μN, amorphous region was also observed just under the surface of the wear traces. As a result of TEM observations after the scanning-scratching tests, it was found that the introduction of dislocation loops or small dislocations took place and no amorphous region appeared, and was also found that several atomic layers at the top surface of the wear traces shifted in parallel to (100). As a result of contrast experiments using TEM, it was found that the dislocation loops which were generated by the both scratching tests were placed in {111}, that is, easy slip plane of Si crystal, and Burgers vectors of the dislocation loops were clarified.

R9.13

The Atomic Scale Removal Mechanism During Chemo-mechanical Polishing of Silicon: An Atomic Force Microscopy Study.

Futoshi Katsuki[1] and Junji Watanabe[2]; [1]Corporate R&D Laboratories, Sumitomo Metal Ind., Ltd., Amagasaki, Japan; [2]Mechanical Engineering and Materials Science, Kumamoto University, Kumamoto, Japan.

Pressure dependence of the microwear of an oxidized Si surface under aqueous electrolyte solutions has been investigated using an atomic force microscope (AFM) with a single crystal Si tip [1]. The removal ratio of Si tip to SiO_2 surface is found to be highly sensitive to the contact pressure. At low pressure, the SiO_2 removal volume in moles is approximately equal to that of Si, while in the high pressure range above 10MPa, the removal volume of SiO_2 is larger than the Si tip removal. These results indicate that, at low pressure, Si-OH of the Si tip surface reacts with Si-O^- of the SiO_2 surface and a formation of Si-O-Si bridge from one Si atom to one SiO_2 molecule at the wear interface. The Si-O-Si bridge weakens the Si-Si backbonds of Si by strong polarization and facilitates a further attack by H_2O molecules, then the Si surface becomes oxidized in the lattice. As the oxidized Si tip scans over the SiO_2 surface, the Si-O-Si bridge and the Si-O backbonds of both the tip and the sample are strained, resulting in bond rupture. The equality of the removal volume both the tip and the sample suggests that the strength of the Si-O-Si bridge is greater than that of the Si-O backbonds, finally, the dimeric silica $(OH)_3Si\text{-}O\text{-}Si(OH)_3$, including the Si-O-Si bridge is dissolved in the KOH solution. On the contrary to this equality, at high pressure, the larger removal volume of SiO_2 than that of Si points to a direct diffusion of H_2O in silica and dissolution takes place at the contact surface, due to an increased liquid temperature and a compressive stress in SiO_2 network. We present a microscopic removal mechanism which is determined by an interplay of the diffusion of water in SiO_2 and Si. [1] F. Katsuki, K. Kamei, A. Saguchi, W. Takahashi and J. Watanabe, J. Electrochem. Soc. 147, 2328 (2000).

R9.14

In-situ Quantitative Nanoscale Metrology for Tribology Process Monitoring.

Antanas Daugela, Norm Gitis, Alex Meyman and Michael Vinogradov; Center for Tribology, Inc., Campbell, California.

Quantitative nanometer scale metrology tools have become a standard in semiconductor and data storage industries, where products are tested for materials properties. It is critical to monitor advanced thin films. A synergy of the nanoscale metrology and manufacturing process and test instrumentation can significantly help in understanding undergoing materials changes. A quantitative nanoscale metrology instrument with in-situ SPM imaging integrated into the tribometer was developed to monitor changes in mechanical properties during tribology tests. Materials properties measurements and surface topography can be assessed at various stages of the test. A 5-um thick Cu coated silicon wafer was tested for changes in material properties during tribology test. Nanoindentation loads of 50 mN to 5 mN were applied. Integrated SPM type imaging and nanoindentation tests revealed changes in material properties such as elastic modulus, hardness and surface topography changes such as roughness at nanometer scale. Dynamics of the copper layer hardening was recorded at several hundreds of time steps during the entire tribology test. As expected, pre-test elastic modulus and hardness measurements indicated presences of the native Cu oxide layer. A multi-dimensional mechanical properties map summarizes wear test quantitative results.

R9.15

Fracture Mechanisms of GaAs Under Nanoscratching.

Jean-Marie Solletti[1], Magdalena Parlinska[1], Ayat Karimi[1], Christophe Ballif[2], Johann Michler[2] and Daniel Schulz[3]; [1]EPFL, Lausanne, Switzerland; [2]EMPA, EMPA, Thun, Switzerland; [3]Bookham, Zurich, Switzerland.

Gallium Arsenide based devices are used widely in photonic and high frequency electronics. After the lithography process, the devices have to be separated. Because of their brittleness, Gallium Arsenide (GaAs) wafers are difficult to machine during processing of optical devices. An alternative solution for separating devices is using cleavage. This can be created by a median crack upon scratching with a diamond tip that will enhance the cleavage process in a specific direction, without generating radial, lateral and oblique cracks and debris that may impede on the cleavage. It is therefore of utmost importance to have insights on the fracture mechanisms of GaAs during the scratching process, in order to promote the median crack over the others defects. In this paper, we reported the influence of the indenter scratch direction on GaAs (001), the applied load and the scratching velocity on the median, radial, lateral and oblique cracks formation. Surface scratch-induced debris and radial cracks were characterized by Atomic Force Microscopy (AFM) and median, lateral and oblique by high-resolution transmission electron microscopy (HRTEM) or AFM. Radial cracks direction were observed on GaAs (001) with direction following the <110> family direction, whatever the scratching direction. Their extension varied linearly with the load to the power of 2/3, from which the fracture toughness was computed. And their density was dependent of the indenter sliding velocity, with low density at high velocity. Median and oblique cracks were observed on GaAs (110) plane. Median cracks followed the <001> direction whereas the oblique ones have a direction forming an angle between 25 and 35° to the GaAs (001) plane. Both slipping and twinning deformations were observed under residual scratches. Fracture mechanisms of radial, median and oblique cracks are discussed in term of GaAs crystallography and on the stress distribution during scratching and compared with fracture mechanism during indentation.

R9.16

Friction and Wear Properties of ALD Coated Micr-electromechanical Systems.

Corina Nistorica[1], J. -F. Liu[1], I. Gory[1], G. D. Skidmore[1], F. M. Mantiziba[2], B. E. Gnade[2] and J. Kim[3]; [1]Zyvex Corporation, Richardson, Texas; [2]University of Texas at Dallas, Dallas, Texas; [3]Kookmin University, Seoul, South Korea.

This study reports the results regarding static friction and wear of coated microelectromechanical systems (MEMS) obtained using thermally actuated tribological test microstructures. Two different types of MEMS thermal actuators were used for direct measurement of static friction between two surfaces: a 50 μm thick silicon on insulator (SOI) - based device and a 3.5 μm thick polysilicon device fabricated in a PolyMUMPS multi-user process. Conformal coatings consisting of 20 nm thick atomic layer deposited (ALD) TiO_2 or ZrO_2 were applied on the microtesters. The effect of film roughness,

velocity, contact area and load as well as the effect of humidity on the static coefficient of friction and wear was studied and compared. Reproducibility of the data was proven by testing multiple devices in parallel. The wear data was quantified from the point of view of debris creation and stability of the friction coefficient. The friction force vs. normal force curves for the oxide covered silicon devices were described by a Johnson-Kendall-Roberts model with pressure-dependent shear strength. The natural oxide covered Si surface as well as the TiO_2 covered surface showed a reduction of the friction force when sliding speed was increased from 14 μm/s to 170 μm/s, and strong dependence on relative humidity which was varied between 0 % and 100 % by placing the test devices in an environmental chamber. The ZrO_2 covered surface showed only a weak dependence on velocity and humidity. Compared to the oxide covered surface, the ZrO_2 coated surface showed a decrease of 30 % in the friction force, while the TiO_2 showed a 10 % decrease in the friction force only at higher relative humidity. The application of ALD coatings resulted in improved reliability of the MEMS devices and decreased wear of the sliding contacts.

R9.17

Elastic Properties of MBE grown Epi-layers on GaSb. Shivashankar Reddy Vangala[1], Kannan Krishnaswami[1], Gregory Griffith[1], Dehua Yang[2] and William D Goodhue[1]; [1]Physics, UMASS lowell, Lowell, Massachusetts; [2]Hysitron Inc, Minneapolis, Minnesota.

Recent interest in antimonide based compound semiconductors for low-power high-speed applications has fostered the molecular beam epitaxial growth of InGaAlAsSb materials-based devices. The eptiaxial layers of the devices are often designed to induce stress and strains that significantly alter the electronic and optical properties of the structure. In order to give feedback to the grower and device designer and achieve the desired control, measurement of the actual stress generated in the epitaxial layers is critical. Over the past two years this group has developed a method to measure the elastic properties of antimonide based materials using microbeams [1]. A quasi-static nanomechanical analyzer was used to obtain load-displacement curves from GaSb microbeams of varying lengths fabricated in a chemical-mechanically polished (100) wafer to extract a directional value (using beam orientation) for Young's modulus of the material. In those experiments we found that the GaSb microbeams behaved more like a "rubbery-type" material, rather than a bulk semiconductor material. Here we report our results from fabricating sets of beams in GaSb epitaxial layers, GaAlSb/GaSb epitaxial layers, and InAsSb ternary antimonide epitaxial layers (all grown on (100) GaSb substrates) and nanomechanically analyzing the results to determine Young's Modulus for each structure. This method is extendable to a variety of other material systems. [1] M. Ospina et al., "Micromechanical characterization of GaSb by microbeam deflection and using nanoprobe and finite element analysis," Mat. Res. Soc. Symp. Proc., Vol. 782, 173-178 (2004)

SESSION R10/T6: Joint Session: Indentation and Phase Transformations
Chairs: William Gerberich and Neville Moody
Thursday Morning, December 2, 2004
Room 202 (Hynes)

8:30 AM R10.1/T6.1

Nanoindentation of SiGe thin films. Jodie E. Bradby[1], James S. Williams[1] and Michael V. Swain[2]; [1]Electronic Materials Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia; [2]Department of Oral Sciences, University of Otago, Dunedin, New Zealand.

The deformation behavior of 150 nm SiGe epitaxial films containing Ge compositions ranging from 9–67 atomic % have been studied as a function of Ge content using nanoindentation and atomic force microscopy (AFM). Initially, the mechanical properties of the films were measured using spherical indenters with a radius down to 1 μm. This revealed no difference in the mechanical response of the films from that of pure Si despite the varying Ge concentrations. However, under the indentation conditions used, the penetration depth was of the order of 50% of the film thickness and the effect of the underlying Si substrate cannot be neglected. To avoid this uncertainty low-load indentation was carried out in a Hysitron (Ubi) nanoindenter using a Berkovich indenter with an effective radius of 70 nm. This resulted in a maximum penetration depth of 30 nm when loaded to 300 μN. The measured mechanical properties remained very similar to that of Si, even at indentation depths of less than one fifth of the film thickness. Cross-section transmission electron microscopy images of residual indents reveal that the films undergo phase transformations during indentation similar to that previously observed in pure Si. Interestingly, however, some subtle differences in the mechanical responses of the SiGe films were observed when compared to the pure bulk Si, with the scatter of the mechanical property data increasing with Ge content. To investigate this further, AFM imaging of the SiGe films revealed a change in the morphology of the surfaces with increasing Ge content. The films containing the highest percentage of Ge were observed to have the highest surface roughness. This is thought to correspond to the density of misfit dislocations caused as a result of the lattice mismatch between the SiGe layers and the Si substrate.

8:45 AM R10.2/T6.2

Spherical Depth-Sensing Indentation on Silicon and Phase Transformation Pressure Dependence on Unloading Rate and Maximum Applied Load. Thomas Frank Juliano, Vladislav V. Domnich and Yury G. Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Many machining operations, including slicing, edge grinding, dicing and ductile regime turning of silicon wafers, lead to pressure-induced phase transformations. These transformations produce a layer of amorphous silicon or metastable phases on the wafer surface which need to be removed by subsequent polishing or etching. Characterizing the effect of localized contact pressure on phase transformations in silicon and other materials through depth-sensing indentation has been shown to be very useful in recent years. Because load and displacement are measured in real time, a wealth of information regarding material response under different loading conditions can be gathered. The rate the indenter tip is unloaded and the maximum applied load on the sample have been previously shown to affect the response of silicon to sharp indentation, but no such study exists for spherical indentation. In this work, a statistical analysis of over 1900 indentations made with a 13.5 μm nominal radius spherical indenter on a single-crystal silicon wafer over a range of loads (25-700 mN) and loading/unloading rates (1-30 mN/s) is presented. The location of the displacement discontinuities on loading and unloading ("pop-in" and "pop-out" events), likely due to pressure-induced phase transformations, is noted as well as pressures at which they occur. Similar to Berkovich indentation, increase in maximum applied load and decrease in unloading rate are seen to raise the average pressure that phase transformations occur on unloading. Multiple occurrences of pop-in and pop-out events are reported for the first time. Raman micro-spectroscopy shows a higher intensity of metastable silicon phases at comparably deeper depth under the surface of the residual impression, where higher shear stresses are present. A stability range for Si-I, Si-II, Si-III, Si-XII and a-Si is found and compared with previous results for Berkovich indentation. Indentation with spherical indenters allows patterning of the wafer surface with new phases of silicon without cracking, which is almost unavoidable in the case of sharp indenters.

9:00 AM R10.3/T6.3

In-situ Characterization of Phase Transformations During Nanoindentation of Deposited and Ion-Implanted Amorphous-Silicon. James S. Williams[1], Jodie E. Bradby[1], Bianca Haberl[1] and Mike V. Swain[2]; [1]Electronic Materials Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia; [2]Department of Oral Sciences, University of Otago, Dunedin, New Zealand.

Recently the deformation behavior of amorphous-silicon (a-Si) has been found to depend critically on both the method of preparation of the amorphous structure and the thermodynamic history of the sample. Whilst some forms of a-Si are significantly softer than crystalline-Si (c-Si) and appear to deform via material 'plastic' flow, annealed a-Si has mechanical properties that closely mirror those of c-Si including phase transformation as the main mode of deformation under indentation. In this study we investigate a range of continuous surface a-Si layers of varying thicknesses produced by both self-ion implantation and deposition techniques. A selection of these samples were annealed (450°C for 30 mins) to create both relaxed and unrelaxed a-Si. The response of the a-Si layers to spherical indentation was studied by in-situ electrical characterization to probe both the onset and depth of penetration of a metallic, high-pressure Si phase during indentation. Results have provided a better understanding of the various modes of deformation and raised some interesting questions relating to amorphous-to-crystalline phase transformations under indentation loading. Discontinuities on both loading and unloading (so-called pop-in and pop-out events), which are associated with phase transformations in c-Si were observed in the annealed (relaxed) a-Si samples but not in the other forms of a-Si. These discontinuities correlated well with the observed onset of a phase transformation. After nanoindentation, the samples were additionally examined using a range of ex-situ techniques including Raman microspectroscopy and cross-sectional transmission electron microscopy to study the end phases (crystalline and amorphous).

9:15 AM R10.4/T6.4

Cross Sectional TEM Studies of Indenter Angle Effects on Indentation-Induced Phase Transformations in Si and Ge.

Songqing Wen[1], James Bentley[1], Jae-il Jang[1,2] and George M. Pharr[1,2]; [1]Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; [2]Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

It is well known that Si and Ge transform to a metallic state under pressure and that other crystalline and amorphous phases can form on the release of the pressure. Many of these same phenomena occur during indentation, making nanoindentation an important tool for exploring pressure-induced phase transformations. Studies have shown that the indentation-induced phase transformations depend on several important parameters including the maximum load, loading rate, and indenter geometry, e.g., whether the indenter is pyramidal or spherical. Here, a new parameter - the centerline-to-face angle of a triangular pyramidal indenter - is explored. Nanoindentations made in single crystals of Si and Ge with a series of pyramidal indenters with tip angles ranging from 35° to 75° were examined by cross-sectional and high resolution electron microscopy. The cross-sectional samples were fabricated to electron transparency using a dual beam focused ion beam mill. By comparing experimental observations with theoretical modeling, the influence of the indenter angle is examined. Results reveal how the phase transformations and deformation mechanisms facilitate the ductile machining of these normally brittle semiconductor materials. * This research was sponsored by the National Science Foundation under grant number DMR-0203552, and by the Division of Materials Sciences and Engineering (SHaRE User Center), U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:30 AM R10.5/T6.5

In-Situ Infrared (IR) Detection of the High Pressure Phase Transformation of Silicon.

John Patten[1], Lei Dong[2] and Jimmie A. Miller[2]; [1]Manufacturing Engineering, Western Michigan University, Kalamazoo, Michigan; [2]Mechanical Engineering, University of North Carolina, Charlotte, Charlotte, North Carolina.

The phenomenon of high pressure phase transformations of semiconductor materials has been extensively investigated over the last 20 years. Previous efforts were mainly focused on studying different phases generated under various loading/unloading conditions using nanoindentation methods. Nanoscratching test however, which more closely resembles a real machining process, has only appeared in a limited number of papers. Additionally, only a very few papers, in addition to the current authors work, show in-situ or direct evidence to establish the existence of this phase change as it occurs. In this paper a new method of in-situ detection of the high pressure metallic phase transformation of semiconductor materials during dead-load scratching is described. This method is based on the simple fact that single crystal silicon is transparent to IR light while metallic materials are not. The sample material used here is silicon, but the same approach can be applied to germanium and other materials, such as ceramics, which have appropriate optical properties. It has been established that silicon goes through a Si-I to Si-II phase transformation under a pressure around 12GPa. This Si-II phase is metallic, which results in absorption of light at IR wavelengths. In this paper experiments are described in which an IR laser-detector system is used in conjunction with a pre-loaded (dead weight) scratching device to detect the metallic high pressure phase of Si. Loads used are 10, 20, 30 and 40 mN. The apparatus is designed so that IR light penetrates a diamond tip, which is a 60 degree conical tip with nominal radius 5um, onto the scratching groove as the tip is translated on the silicon wafer. The IR diode laser used here is an 8mw Infrared laser with a wavelength of 1330 nm. An Infrared detector is placed below the silicon wafer to sense the transmitted IR light. Results show a decreasing trend of voltage (IR transmittance) after each scratch and an average of 10% decrease after 4 scratching cycles in the same groove. This indicates that a metallic phase has been generated during scratching and the metallic phase has preferentially blocked the IR laser light. Results also show that the as the load in increased the measured signal change increases, indicating a greater amount of transformed metallic silicon AFM and SEM have been used to measure the grove shape and study the chips generated in the pile-up area. These images show that ductile deformation, for the loads investigated, correlate with the generation of the metallic silicon during simulated machining.

9:45 AM R10.6/T6.6

Abstract Withdrawn

10:30 AM *R10.7/T6.7

High Pressure Surface Science and Engineering.

Vladislav Domnich, Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

In majority of mechanical applications of materials, their surface experiences a contact with another material and takes the external load before the bulk of the material is influenced. In some cases, surface interactions influence the bulk (e.g., propagation of cracks, dislocations or point defects from the surface in depth). In many cases, only the outermost surface layer is affected by the surface contact with no detectable changes in the bulk of the material. We are primarily concerned in this review with that kind of interactions. The thickness of the surface layer affected by the external mechanical forces ranges from nanometers to micrometers. Thus, in our case, the definition of "surface" is different from the one used by surface scientists. We need to introduce an engineering definition of the surface as the outermost layer of the material that can be influenced by physical and/or chemical interaction with other surfaces and/or the environment. During contact interactions, a harder object can leave imprints on the material surface. In particular, when a hard indenter (e.g., diamond) touches the surface of another hard material (ceramic or semiconductor), very high pressures (up to one megabar) can be achieved under the indenter because the contact area in the beginning of the penetration of the indenter into material is small. These pressures can exceed the phase transformation pressure for many materials. Understanding and appreciation of this fact can help to understand the mechanisms of wear, friction and erosion. High shear stresses and flexibility of contact loading conditions allow one to drive phase transformation that cannot occur under hydrostatic stresses, or would occur at much higher pressures. We will describe phase transformations and amorphization that occur in many semiconductors under contact loading such as indentation with hard indenters or scratching, grinding, milling, etc. Contact loading is one of the most common mechanical impacts that materials experience during processing or application. Examples are cutting, polishing, indentation testing, wear, friction and erosion. This kind of loading has a very significant nonhydrostatic component of stress that may lead to dramatic changes in the materials structure, such as amorphization and phase transformation. Simultaneously, processes of plastic deformation, fracture and interactions with the environment and counterbody can occur. The latter have been described in numerous publications, but the processes of phase transformations at the sharp contact were investigated only during past decade and the data obtained have never been summarized. This problem is at the interface between at least three scientific fields, namely materials science, mechanics and solid state physics. Thus, an interdisciplinary approach will be used to describe how and why a nonhydrostatic (shear) stress in the two-body contact drive phase transformations in materials.

11:00 AM R10.8/T6.8

Constant and Ramped Load Nano Scratch Test Behavior of Impregnated Hard Multilayer Coatings.

Bala Kailasshankar, Devdas Pai, Sergey Yarmolenko and Jag Sankar; Center for Advanced Materials and Smart Structures, Dept of Mechanical Engg, North Carolina A&T State University, Greensboro, North Carolina.

Impregnated hard multilayer chromic oxide based coatings produced on 9.5 mm 1018 square steel bars were studied using microhardness and nanoscratch techniques. Constant and ramped load nano scratch tests were done using a MTS Nano Indenter XP system. The dependence of the residual wear depth, profile height and friction coefficient on load are compared in constant and ramped load test conditions. The impregnated hard coatings show less permanent damage, lower friction coefficients and lower pileup heights than untreated steel under the same load conditions.

11:15 AM R10.9/T6.9

Micro-Raman Mapping and Analysis of Indentation-Induced Phase Transformations in Germanium.

Jae-il Jang[1,2], M.J. Lance[2], Songqing Wen[1] and G. M. Pharr[1,2]; [1]The University of Tennessee, Knoxville, Tennessee; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Through a number of theoretical studies and diamond anvil cell experiments over the past four decades, it is now well accepted that germanium transforms under pressure from the normal diamond cubic phase (Ge-I) to the metallic beta-tin phase (Ge-II) at about 10 - 11 GPa and re-transforms to Ge-III (st12 structure) or Ge-IV (bc8 structure) during release of the pressure. Since these transformations are broadly analogous to those occurring in silicon, one might expect the indentation-induced phase transformations in these two materials to be approximately the same. However, in comparison to Si, the number of experimental studies that have examined indentation behavior of Ge is relatively small. This study was undertaken to answer to address several key unresolved questions. Nanoindentation experiments were performed (100) Ge single crystals using a series of triangular pyramidal indenters with different tip angles, including the common Berkovich and cube-corner indenters. Although, in contrast to Si, none of the indentation load-displacement curves indicated

pop-out or any pronounced shape change, micro-Raman spectroscopy in conjunction with scanning electron microscopy provided positive evidence that phase transformations involving amorphous and crystalline phases do indeed occur. In addition, the observations suggest that the indenter geometry significantly affects the transformation behavior. Micro-Raman mapping techniques were used to better understand the phenomena and evaluate the post-indentation stress distribution. Results are discussed in terms of prevailing descriptions of phase transformation in Ge and how the transformations progress and affect deformation during nanoindentation. * This research was sponsored by the National Science Foundation under grant number DMR-0203552, and by the Division of Materials Sciences and Engineering (SHaRE User Center), U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

11:30 AM R10.10/T6.10

Nanomechanical Properties of Metal Surfaces Containing He Bubbles. James A. Knapp, David M. Follstaedt and Samuel M. Myers; Sandia National Laboratories, Albuquerque, New Mexico.

The mechanical properties of surfaces can be dramatically affected by a dispersion of fine precipitates such as is produced by ion implanting insoluble species. We previously formed nanometer-size precipitates of hard oxides (NiO, Al_2O_3) in implanted Ni and produced surface layers with yield strengths as high as 5 GPa (Follstaedt et.al, Mat. Trans. A, 2003). Here we examine the strengthening that can be achieved with small bubbles, which are shearable precipitates, formed by implanting He into Ni under several conditions to study the effects of varying bubble size and concentration. This treatment could be used to engineer hard surface layers, and the results are also of interest for understanding the effects of He build-up due to tritium decay in metal tritide films used in neutron tubes. In Ni implanted with 5 at.% He to a depth of 600-700 nm at room temperature, cross-section TEM shows a dispersion of He bubbles with diameters of 1 nm or smaller. Using nanoindentation combined with detailed finite element modeling to separate layer properties from the substrate, the bubble-containing layer is found to have a yield strength of 2.4 GPa, nearly 7 times that of the underlying Ni. This pronounced strengthening is ascribed to the retardation of dislocation glide by the bubbles, an effect arising from the combined influences of image forces, gas pressure, and step energies associated with dislocation cutting. Initial estimates indicate that the retarding effect for the small bubbles approaches that necessary to prevent passage of the dislocation through the bubble, and, in fact, an assumption of Orowan hardening gives a flow stress of 2 GPa, comparable to what is observed. We have numerically solved the continuum strain equations for dislocations moving in a three-dimensional periodic array of pressurized bubbles, and are using this model to interpret the observed mechanical behavior at a more quantitative level. When the same He concentration is implanted at 500 C, the bubbles are much larger at 5 nm in diameter and the hardness of the layer is 40% lower, though still substantially higher than untreated Ni. The bubble layers also show signs of abrupt yielding in shear at depths of 100 nm during the indentation; notably, the shear stresses at failure are relatively modest (1.3 GPa) when compared to Ni containing Al_2O_3 precipitates, where the layer can withstand 3 GPa shear stress without failure. 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.

11:45 AM R10.11/T6.11

Dependence of Hardnesses on Band Gaps and Polarizabilities. John Joseph Gilman, MSE, UCLA, Los Angeles, California.

Hardness depends on the strength of bonding in solids. Therefore, it depends on the type of bonding: covalent, metallic, ionic, or dispersion. The micro-mechanism of the deformation that occurs during indentation (or scratching) involves either the motion of glide dislocations or a phase transformation (twinning is taken to be a mono-molecular phase transformatiom), or both. In pure simple metals, the mobilities of individual dislocations on the primary glide systems are indefinitely large since the bonding is non-local. A result of the non-local bonding is that the energies of the cores of the dislocations are independent of their positions so no static forces resist their motion. In this case, their motion is limited only by electron and/or phonon viscosity. Therefore, the deformation associated with indentation is only resisted by strain-hardening (dislocation dipoles), and by the need for deformation on the higher order glide systems. The same is true for high-purity alkali halide crystals. However, in covalent crystals the behavior is quite different because the bonding is localized. In them, dislocation motion (via the motion of localized kinks) requires the promotion of valence (bonding) electrons into conduction (anti-bonding) states. The energy required is that of the minimum band gap. But a kink has an associated volume. Therefore, the overall deformation process depends on the energy-gap density. For the hompolar (Group IV) crys- tals, as well as the isoelectronic III-V srystals, this observed exp- erimentally. The situation is somewhat more complex for the hetero- polar III-V crystals because ionic charge centers play a role in them. Band gaps are related to polarizabilities, and to shear moduli so there are some additional links between hardnesses and electronic properties that are discussed.

SESSION R11: Modeling, Simulation and Analysis of Indentation Data
Chairs: Marc Fivel and Nigel Jennett
Thursday Afternoon, December 2, 2004
Room 202 (Hynes)

1:30 PM R11.1

Multiscale Simulation of Dynamic Nanoindentation and Cyclic Plasticity at Finite Temperature. Behrouz Shiari and Ronald E. Miller; Mechanical and Aerospace Engineering, Carleton University, Ottawa, Ontario, Canada.

Modeling dynamic nanoindentation and cyclic plasticity requires explicit retention of atomic-scale details but are also strongly influenced by, for instance, dislocations and their motion (plasticity) at the micron and larger scales. To handle these multiple scales simultaneously, a new modified version of the Coupled Atomistic and Discrete Dislocation (CADD) method is used to investigate the nucleation and dynamics of dislocations during dynamic nanoindentation and cyclic plasticity of a two dimensional lattice system at finite temperature. The Dynamic CADD model simultaneously captures the atomistic mechanisms and the long range effects without the computational cost of full atomistic simulations, and permits the simulation of system sizes that are approaching experimentally accessibly systems. The load-displacement (load/unload) curves for different temperatures are compared for a constant indenter velocity. Our technique allows us to observe the initial nucleation of dislocation in atomistic region, below the surface of the indented crystal, and then correlate features in the load-displacement behviour of the indenter with the motion, cross-slip and pile-up of dislocations. Results of hardness versus indentation depth reveal a strong size effect in the plastic response. Finally, further load/unload cycles have been performed to study the damage evolution under cyclic deformation. The simulation reveals several features, such as the dislocation density per cycle, that could give rise to fracture initiation.

1:45 PM R11.2

Modeling Indentation in Linear Viscoelastic Solids. Yang-Tse Cheng[1] and Che-Min Cheng[2]; [1]Materials and Processes Lab, General Motors Research and Development Center, Warren, Michigan; [2]Institute of Mechanics, Beijing, China.

Using a scaling approach we provide a new derivation of the load-displacement relationship for conical and pyramidal indentation in liner viscoelastic solids of constant Poisson's ratios. We then examine several methods for obtaining viscoelastic properties from loading curves under conditions such as constant displacement rate, constant indentation strain rate, and quasi-step loading. Equations are derived for indentation in three-parameter "standard" viscoelastic solids. These equations can be used to help select appropriate indentation conditions for determining viscoelastic properties. We have also conducted numerical calculations of indentation in linear-viscoelastic solids with time dependent Poisson's ratios. The analytical and numerical results provide new insights into questions about determining contact depth, the necessity of a holding period between the loading and unloading steps, and the significance of constant indentation strain rate measurements.

2:00 PM R11.3

The Study of Dislocation Nucleation at Surface Heterogeneities by Combined Atomistic and Continuum Approach. Guanshui Xu[1], Chengzhi Li[1] and Darren Segall[1,2]; [1]Department of Mechanical Engineering, Univ. of California, Riverside, Riverside, California; [2]Department of Applied Physics, California Institute of Technology, Pasadena, California.

Dislocation nucleation at surface heterogeneities has been one of the major concerns in the development of nanoscale electronic devices. The phenomenon is an atomic process, and in general needs to be treated by an atomic approach. Direct atomistic simulation, however, is ineffective in determining the energetics of dislocation nucleation because of the involvement of large amount of atoms in unstable saddle point configurations. By incorporating minimum atomic information into a continuum approach, the formulation of the Peierls-Nabarro dislocation model into the variational boundary integral method offers an alternative effective approach to tackle this important problem. Our recent study based on this approach has

indicated that atomic scale steps have significant effects on dislocation nucleation from the stressed crystal surface. Because of the much debated approximation involved in the Peierls-Nabarro dislocation model, it is important to validate or corroborate this result with other more direct atomic simulations. We achieve this goal through the following multiscale modeling and simulation. Using tantalum as an example crystal, we first validate a quantum mechanics based interatomic potential by calculating the generalized stacking fault energy using both the quantum mechanics and this interatomic potential. The obtained generalized stacking fault energy based on the interatomic potential is then used to model the potential between the two adjacent atomic planes along the slip direction which needs to be incorporated into the Peierls-Nabarro dislocation model. In a relatively simple configuration, dislocation nucleation is studied by the Peierls-Nabarro model and the direct atomic simulation, respectively. By comparing the critical conditions for dislocation nucleation obtained by both methods, we intend to corroborate the result obtained by the Peierls-Nabarro dislocation model, therefore justify using it for more complicated dislocation problems.

2:15 PM R11.4
Determination of Plastic Properties of Metals by Nanoindentation - Experiments and Finite Element Simulations. Karsten Durst, Bjoern Backes and Mathias Goeken; Materials Science, University Erlangen, Erlangen, Germany.

Obtaining physically defined macroscopic mechanical properties like yield strength and work hardening coefficient of metals directly from nanoindentation data requires the analysis of the indentation process and the evaluation methods. A crucial point in the analysis of the load-displacement-curves is the determination of the contact area. Depending on the work hardening behaviour, the contact area is underestimated and thus a too high hardness value is determined from the indentation test. To address these subjects, nanoindentation experiments were performed on annealed conventional copper and brass and on ultrafine-grained (UFG) copper and brass. Ultrafine-grained cooper deforms nearly perfectly-plastic, whereas the annealed materials strongly work-harden during deformation. The macroscopic mechanical properties of the samples were determined by uniaxial tension/compression tests and different work hardening states were realized by pre-straining the material. The indentation tests were performed using the continuous stiffness option of the Nanoindenter XP. All indentation tests were carried out using a cubecorner and a Berkovich tip, applying thus, according to Tabors theory on representative strain, different amount of plastic strain to the material. The experimental work was complemented by finite element simulation using the compression test data as input data for the simulations. In the simulations, the contact area was determined directly from the finite element mesh and by evaluating the load-displacement-curves. Atomic force microscopy was used to image the residual impressions of the indentations. We find that the work hardening behaviour influences the calculated hardness. UFG-copper, which deforms elastic-perfectly plastic, shows a strong pile-up, resulting in too high Oliver/Pharr hardness values. The hardness as determined by cubecorner and Berkovich-indenter is about the same. Around the indentations of the annealed state of the conventional materials, only a small amount of pile-up was found. The cubecorner-hardness is much higher as the hardness determined by Berkovich-indentation. Moreover we find, depending on the indentation depth and pre-straining of the material a good agreement in between experimental and simulated load-displacement curves for both indenter geometries. From the experiments and simulations, the representative strain is calculated for the two indenters, using the real contact area as determined by finite element simulations. A constraint factor of 2.9 is found for most cases. These results allow the reconstruction of the macroscopic stress-strain curve using the Berkovich and cubercorner hardness value at the corresponding strain level. This concept is not easily applied to the Oliver/Pharr hardness, because the real contact area depends on the work hardening behaviour of the material, which changes during deformation. Using Oliver/Pharr hardness, we find a constraint factor in between 3.8-4.6.

2:30 PM R11.5
Conical Indentation of Anisotropic Materials: An Exact Solution. John Greg Swadener, MST-8, Los Alamos National Laboratory, Los Alamos, New Mexico.

Indentation of ceramic materials is often used for calibration of nanoindenter tips and instruments. However, ceramic single crystals that are used for indenter tips and calibration substrates are anisotropic, and determining the tip shape by fitting numerical solutions requires a large amount of trial and error. General exact solutions are available for spherical contact, but not for conical indenters, which give a close approximation to the widely used Berkovich and Vicker's indenter tips. Based on their spherical contact solution, Swadener and Pharr (2001, Phil. Mag. A, v81, 447) developed an approximate solution for conical indentation of general anisotropic materials. However, this was shown by Vlassak et al. (2003, J. Mech. Phys. Solids, v51, 1701) to be exact only for a particular type of anisotropic material. Vlassak et al. developed a general approximate solution with greater accuracy. While these approximate solutions are useful, they cannot determine the accuracy of the result or guarantee that an exact solution exists. Here an exact solution is developed for conical indentation of general anisotropic materials. The exact solution serves to check the accuracy of the approximate methods. For sapphire, it is found that the approximate solutions give an indentation modulus within 1% of the exact values at various orientations. This research was sponsored by the United States Department of Energy, Office of Basic Energy Sciences.

2:45 PM R11.6
Modeling of Conical Indentation in Thin Films on Substrates. Wangyang Ni and Yang-Tse Cheng; Materials and Processes Lab, General Motors Research and Development Center, Warren, Michigan.

Dimensional analysis and finite element modeling were conducted to examine conical indentation in hard films on soft substrates. The limitations of the Oliver-Pharr method were examined. A simple linear relationship between the ratio of hardness to reduced modulus and the ratio of reversible work to total work was observed for conical indentation in coated materials. This relationship is an extension of previously reported relationships between the work of indentation, hardness, and elastic modulus for indentation in homogeneous materials [1-3]. Together, they form the basis for analyzing instrumented indentation experiments using the concept of reversible and irreversible work of indentation. [1] Y.-T. Cheng and C.-M. Cheng, Appl. Phys. Lett. 73, 614 (1998). [2] Y.-T. Cheng, Z. Li, and C.-M. Cheng, Phil. Mag A 82, 1821 (2002). [3]W. Ni, Y.-T. Cheng, C.-M. Cheng, and D. S. Grummon, J. Mat. Res. 19, 149 (2004).

3:30 PM *R11.7
An Energy Balance Criterion for Small Volume Plasticity. William Warren Gerberich, William M. Mook and Megan J. Cordill; Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN., Minnesota.

Hardness or flow strength for small volume plasticity is addressed using dislocation models. If one equates the stored elastic energy change being absorbed by plastic energy dissipation, one obtains an incorrect dependence on the radius and depth of penetration. This pertains to either spherical tip indentation or spheres under compression. One way around this is to invoke an instability criterion. Prior work has shown multiple yield excursions, typically called stair-case yielding, associated with either dislocation nucleation and/or dislocation pile-up induced oxide film rupture. We will review some of these observations in Au, Cu, Al, Fe, W, Si and SiC. As shown by Curtin, Suresh, Wolf and others, these instabilities are observed in atomistic simulations as well. With an instability criterion including surface effects, a range of plasticity observations may be predicted for both types of spherical geometries as well as nanoboxes. The latter involves thin-walled Au boxes that can be shown to have a load bearing capacity for plastic deformation which exceeds solid spheres or cubes. Implications to the length scales used in modeling small volume plasticity are discussed. For example, if one considered flow strength only, then an indenter with the same tip radius as a nanosphere should always have a greater flow strength than the nanosphere. This would particularly be the case at very small depths where constraining influences on the sphere are negligible but large on the indenter. However, by including surface effects the opposite is predicted and observed for nanospheres in the 20 to 100 nm diameter range.

4:00 PM R11.8
Simulation studies of the role of grain boundaries during the nano-indentation of Ni. Diana Farkas[1] and Ho Jang[2]; [1]Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia; [2]Materials Science and Engineering, Korea University, Seoul, South Korea.

Molecular dynamics simulations of nano-indentation were performed on a Ni bi-crystal containing a S = 5 (210) grain boundary parallel to the free surface being indented. In these simulations, Shockley partial dislocations were nucleated beneath the indenter and propagated along the {111} slip planes until they reached the grain boundary. The grain boundary stopped the propagation of the dislocations and only at later times dislocation activity was observed in the second grain beneath the indenter. The effect of the grain boundary was to lower the indentation speed and dislocation motion during nano-indentation, with respect to identical conditions in a single crystal. The results are compared with simulations in polycrystals where the grain boundaries of more general character are also shown to emit dislocations.

4:15 PM R11.9
Modeling of Nanoindentation and Microstructural Ductile Behavior in Metallic Material Systems. Mohammed A. Zikry[1], Jeong Ma[1], Waeil Ashmawi[1], Dave Schall[2] and Donald Brenner[2]; [1]Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC, North Carolina; [2]Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina; [3]Materials Science and Engineering, North Carolina State University, Raleigh, NC, North Carolina; [4]Materials Science and Engineering, North carolina State University, Raleigh, NC, North Carolina.

Specialized large-scale computational finite-element and molecular dynamic models have been used to understand and predict how dislocation-density emission and contact stress fields due to nanoindentation affect inelastic deformation and failure evolution at scales that span the molecular to the continuum level in ductile systems. Dislocation-density distributions and local stress fields have been obtained for different crystalline slip-system orientations. These evolving local stress fields are used to track how indentation at different scales and the evolving stress states affect thermo-mechanical strength and indentation depth and plastic zone size. The interrelated effects of grain boundary orientation and shape, dislocation-density pile-ups and evolution, lattice parameter mismatches, interfacial energies, and crystalline structure on indentation inelastic regions have been investigated.

4:30 PM R11.10
An Analytical Approach for Relating Hardness and Yield Strength for Materials with High Ratio of Yield Strength to Young Modulus. Luc Jean Vandeperre, Finn Giuliani and William John Clegg; Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Hardness testing is a straightforward way to characterise the mechanical properties of hard, brittle, materials. For rigid ideally plastic materials, Tabor showed that the hardness, H, is about three times the yield strength, Y, consistent with experimental results. However, for materials with a high ratio of Y to the elastic modulus, E, experimental data show that this is incorrect with the ratio of the hardness to the flow stress decreasing toward one as Y / E increases. This behaviour is predicted by finite element calculations but to date analytical expressions have not been able to correctly predict the relation between Y and H nor have they been able to show how the geometry of the indenter is important. Therefore, in this paper the correlation between H and Y for such materials is re-examined using an analytical approach to provide a physical interpretation, which explains the trends observed. It is shown that existing analytical predictions using the analogy of the spherical cavity fail to reproduce experimental and finite element results because the accommodation of the intrusion of the indenter due to surface deformation is not taken into account, while experiments made here and elsewhere indicate that the latter can be substantial. A simple modification is proposed, which accounts for this, and gives a reasonable prediction of the relation between hardness and yield strength for materials, which have a well determined yield point and do not strain harden. The treatment also gives an explanation for the effect of indenter geometry on measured hardness for such materials. The relevance of the proposed mechanism for the measurement of hardness is discussed and compared with experimental results.

4:45 PM R11.11
The Mechanics of Indentation Induced Lateral Cracking. Xi Chen[1], John W. Hutchinson[2] and Anthony G. Evans[3]; [1]Civil Engineering and Engineering Mechanics, Columbia University, New York, New York; [2]Harvard University, Cambridge, Massachusetts; [3]University of California, Santa Barbara, California.

The mechanics governing the lateral cracks that form when a hard object plastically penetrates a ceramic is presented. The roles of indentation load, penetration depth and work of indentation are all highlighted, as are the influences of the mechanical properties of the substrate. A closed form solution for cracking induced by expansion of a two dimensional cavity is used bring out essential features related to parametric dependence and scaling. The three dimensional axisymmetric problem for an annular crack driven by a rigid spherical or conical indenter pushed into a semi-infinite half-space of elastic-perfectly plastic material is solved using numerical methods. The region of highest tensile stress is identified corresponding to the location where a crack is most likely to nucleate. This location coincides with the depth below the surface where the crack will expand parallel to the surface under mode I conditions. The solutions have been validated by comparison with measurements of the cracks that form upon Vickers indentation. The basic formula for the crack radius has been used to predict trends in cracking upon static penetration and impact by a projectile. In both cases, cracking is diminished by increasing the toughness of the ceramic and by diminishing its yield strength.

SESSION R12: Nanomechanics of Structurally Graded Materials and Thin Films
Chairs: John Swadener and Krystyn Van Vliet
Friday Morning, December 3, 2004
Room 202 (Hynes)

8:30 AM *R12.1
Nanoindentation Studies of the Effects of Nano-Scale Structural Features on Mechanical Response. Subra Suresh, Materials Science and Engineering, MIT, Cambridge, Massachusetts.

This presentation will provide a summary of recent experimental work on the use of depth-sensing nanoindentation and nanoscratch for the systematic and controlled determination of the effects of ultrafine scale structural features on a variety of mechanical responses. Specific issues addressed will include: (a) changes to the strength, ductility and rate-sensitivity of mechanical deformation as the grain size of a metal is decreased from micrometer to nanometer scale, (b) the enhanced rate-sensitivity of deformation arising from the introduction of nano-scale twins within polycrystals, (c) alternations to the tribological contact and sliding contact fatigue resistance through grain refinement in nanostructured materials, and (d) the effects of controlled gradients in structural feature dimensions on the resistance to nanoindentation. In addressing each of these topics, systematic comparisons in mechanical responses will be made, wherever appropriate, among well-controlled and well-characterized model material systems with micro, ultrafine and nano-scale structural features. Some general observations will also be presented on the significance and limitations of the use of depth-sensing nanoscale contact for the probing of ultrafine scale structural effects on mechanical response.

9:00 AM R12.2
An Investigation of Non-linear Stress-strain Behavior of Thin Metal Films. Norbert Huber[1], Thorsten Dietz[1] and Eduard Tyulyukovskiy[2]; [1]Institut fuer Materialforschung II, Forschungszentrum Karlsruhe, Karlsruhe, Germany; [2]Institut fuer Zuverlaessigkeit von Bauteilen und Systemen, Universitaet Karlsruhe (TH), Karlsruhe, Germany.

The stress-strain behaviour of thin metal films is of significant importance for the design and reliability assessment of micro-electronic and micro-mechanical systems. For a basic study various metal film/substrate systems were investigated. They are composed of all possible material combinations using Ti, Cu, and Al for the film and the substrate, respectively. Each film material was deposited by sputtering on all three substrate materials at the same time with film thicknesses from 1 micron to 4 microns. The non-linear stress-strain curves of the films were determined from nanoindentation experiments with a pyramidal indenter. The measured load-depth data are analysed using the method, developed by Huber et al. [1], and is based on neural networks. An inverse mapping of depth-dependent dimensionless hardness and stiffness data yields the material parameters describing a non-linear elastic-plastic stress-strain curve of Armstrong-Frederick type. Suppositions for the application of this method are a sufficiently different hardness between film and substrate, and available hardness and depth data for a depth range from 0.1 to 1.5 times of the film thickness. This allows to destroy the self-similarity of the pyramidal indent and to collect enough data for a separation of film and substrate properties. For all film materials a significant thickness dependence in strength has been observed. In addition, a remarkable difference in strength for identical film materials and thicknesses was found with different substrate materials. Using focussed ion beam microscopy, it is shown that the microstructure of the films depends strongly on the substrate material and is well correlated with the observed film strengths. [1] N. Huber, W.D. Nix, H. Gao: Identification of elastic-plastic material parameters from pyramidal indentation of thin films, Proceedings of the Royal Society London A, Vol. 458, pp. 1593-1620, 2002.

9:15 AM R12.3
Nanoindentation of Multilayer PZT/Pt/SiO2 Thin Film Systems on Silicon Wafers for MEMS Applications. Chibisi Chima-Okereke, Mike J. Reece and Andrew J. Bushby; Materials, Queen Mary University of London, London, United Kingdom.

The mechanical properties of PZT multilayer systems have become increasingly important in applications for MEMS devices. Nanoindentation is a promising tool for obtaining the elastic properties of thin films. However, no means exists to obtain the elastic modulus of the PZT in the multilayer system. Indentation modulus measured in multilayered materials is a composite modulus dependent

on the mechanical properties of all the layers in the system and the depth of penetration. The indentation modulus vs. a/t behaviour of various thicknesses of multilayered PZT/Pt/SiO2/ on silicon wafer film systems using a range of indenter radii, were investigated and compared with finite element models and a new analytical solution. Six different PZT film thicknesses were indented (70, 140, 350, 700, 1500, and 2000 nm), and four indenter radii were used (3, 10, 20 and 30 μm). The behaviour of the substrate when the SiO2 layer was removed was also investigated. Good agreement was shown between FEA, analytical equations, and experimental data. Indentation modulus behaviour with depth was found to be complex and obtaining the modulus of the top layer is far from straight foward.

9:30 AM R12.4
Microbridge Nanoindentation testing of Plasma Enhanced Chemical Vapor Deposited Silicon Oxide Films. Zhiqiang Cao and Xin Zhang; Manufacturing Engineering, Boston University, Brookline, Massachusetts.

Plasma-enhanced chemical vapor deposited (PECVD) silane-based oxides(SiOx) have been widely used in both microelectronics and MEMS (MicroElectroMechanical Systems) to form electrical and/or mechanical components. During fabrication of such microelectric and MEMS devices, PECVD SiOx undergo many thermal cycles, which often causes unwanted changes in thermal-mechanical properties of the material, and consequent degradation of device performance and reliability. In this paper, a novel nanoindentation-based microbridge testing method for thin films is proposed to measure both the residual stresses and Young's modulus of PECVD SiOx thin films. Our theoretical model used a closed formula of deflection vs. load, considering both substrate deformation and residual stress in the thin film. Freestanding microbridges made of PECVD SiOx thin films were designed and fabricated using bulk micromachining techniques. To simulate real thermal processing in device fabrication, these microbridges then underwent various rapid thermal annealing (RTA) at temperatures ranging from 100°C to 800°C. An interferometric microscope was also used to measure the curvature profiles of the bridges. Together with nanoindentation test results on the microbridges, we were able to decide the changes in residual stresses and Young's modulus of the PECVD SiOx thin films under different thermal annealing. Two factors, density change and plastic deformation, were identified as controlling mechanisms of stress changes in the films. A microstructure based mechanism elucidates "seams" as source of density change and "voids" as source of plastic deformation, accompanied by viscous flow. This mechanism was applied to explain our experimental results of thermal annealing of PECVD SiOx films.

9:45 AM R12.5
Elastic and Plastic Behavior of Niobium with Niobium Pentoxide Surface Films. Christelle Callamand[1], Vijay Sethi[2] and Ronald Gibala[1]; [1]Materials Science & Engineering, University of Michigan, Ann Arbor, Michigan; [2]Western Research Institute, Laramie, Wyoming.

The elasic and plastic behavior of niobium single crystals coated with anodically-deposited amorphous thin films of niobium pentoxide of thicknesses up to 300 nm has been determined by nanoindentation techniques at room temperature. These results have been compared to ones obtained for the same materials in tension and compression experiments at lower temperatures and strain rates. The oxide films deform compatibly with the niobium substrate, with the operative deformation mechanism in the oxide films being shear banding. The hardnesses of the film and the substrate are 12 GPa and 0.9 GPa, respectively. The Young's moduli are 180 GPa and 110 GPa, respectively. At indentation depths below approximately 600 nm, the film-coated niobium is harder than the corresponding uncoated material, consistent with constraints offered by the formation of geometrically necessary dislocations under the indenter tip. At much larger indentation depths, such as 6000 nm, involving larger plastic zone sizes, the film-coated niobium is softer than the same uncoated material. These latter results are consistent with ones on the same materials deformed over larger length scales in tension or compression at lower temperatures and strain rates. The softening behavior is well explained in terms of enhanced dislocation nuleation into the niobium substrate from the film-substrate interface.

10:30 AM *R12.6
Strain Rate Sensitivity in Nanocrystalline and Ultrafine-grained fcc Metals as Investigated by Nanoindentations. Mathias Goeken, Materials Science, University Erlangen-Nuremberg, Erlangen, Germany.

The mechanical properties of bulk nanostructured metals in the grain size region of 20-500 nm is investigated by nanoindentations in comparison with conventional measurements on bulk samples. Besides hardness and Young's modulus measurements, the nanoindentation method allows also controlled experiments on the strain rate sensitivity, which are discussed in detail in this paper. Nanoindentation measurements in a Nanoindenter XP can be performed at indentation strain rates between 10-3 s-1 and 0.1 s-1. A nanoindentation system in combination with an atomic force microscope (NI-AFM) allows very local measurements of the mechanical properties. The ultrafine-grained materials with a grain size between 200 - 400 nm are produced by severe plastic deformation. Nanocrystalline metals with a grain size below 100 nm are produced by pulsed electrodeposition or a combination of inert gas condensation and high pressure torsion. The fcc metals Al, Cu, Ni, and Pd were investigated. Especially nanocrystalline metals with a relative low melting point as Al and Cu show a significant strain rate dependence at room temperature in comparison with conventional grain sized materials even with a ultrafine-grained microstructure. Inelastic effects are found during repeated unloading-loading experiments in nanoindentations. The nanoindentation technique allows also studying the mechanical properties in shear bands which often develop during fatigue loading. Nanoindentation experiments at different strain rates are compared with tensile experiments which show a similar strain rate influence. The nanoindentation measurements on the elastic properties are compared with dynamic measurements of the resonance frequencies of bulk samples. The origin of the strain rate dependence and of the inelastic deformation behaviour is discussed in terms of thermally activated grain boundary relaxation mechanisms.

11:00 AM R12.7
Investigation of Indentation Methods For Properties Determination In Hard Film/Soft Substrate Systems . Marian S. Kennedy[1], Scott P. Anderson[1], David F. Bahr[1] and Neville R. Moody[2]; [1]School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington; [2]Sandia National Laboratories, Livermore, California.

The development of new film systems for microelectronic, micromechanical and nanomechanical applications brings the need for accurate and reproducible measurement of their mechanical properties. Although both traditional quasistatic and dynamic indentation testing techniques yield comparable results for hard films and hard substrates, the integration of soft films and substrates introduces the need to consider dynamic response of soft materials such as creep in both traditional and dynamic measurements. A comparison of traditional quasistatic indentation measurements and dynamic methods with sinusoidal cycling has been made on hard film/soft substrate systems to determine the quantitative difference between measurement techniques and the effects of viscoelastic deformation in the underlying material. The systems include compressively stressed tungsten films on SU-8 polymer, compressively stressed tungsten on platinum films, and tensile stressed lead-zirconate- titanate (PZT) on platinum. The response to indentation varied with film system. The first system exhibited a definite viscoelastic response, while the second exhibited strong effects of creep. Indentations into the PZT on platinum film using the dynamic method showed significant regions of pile-up from the underlying platinum film which were not present under quasistatic indentation, however at very shallow depths the modulus of PZT could be determined using the dynamic technique. Indentations into the compressively stressed tungsten on platinum showed a different morphology than the tensilely stressed PZT. Viscoelastic effects clearly impacted the compressively stressed films on the SU-8. These results will be discussed in terms of the effects of compressive and tensile overlayers on properties measurements, particularly on the differences between the dynamic and static techniques and the effects of pile up on both methods. 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.

11:15 AM R12.8
Non-Destructive Measurement of Thickness or Density of Thin Coatings by a Combination of Instrumented (Nano) Indentation and Acoustical Techniques. Nigel M. Jennett, Giles Aldrich-Smith and Anthony S. Maxwell; Div. Engineering and Process Control, National Physical Laboratory, Teddington, Middlesex, United Kingdom.

Nanoindentation is one of the very few techniques that can measure both the elastic and plastic properties of very small volumes of materials. Nanoindentation can now be used to determine the plane strain elastic modulus of sub-micron thickness coatings (~200 nm) with a low uncertainty, even when the normal indentation response includes a significant component from the substrate. The theory underpinning acoustical measurements (impact resonance and surface acoustic wave spectroscopy) requires knowledge of elastic modulus, thickness, density and Poisson/s ratio to describe the material response. If suitable measurements of these parameters for a substrate and a coating are combined, a self-consistent and self-validating set of

mechanical properties for thin coatings can be obtained. We describe here a combination of Nanoindentation and acoustical test methods in which nanoindentation is used to measure the coating plane strain elastic modulus (a composite of Young/s modulus and Poisson/s ratio) and Surface acoustic wave spectroscopy is used to measure the velocity dispersion of surface acoustic waves through the coated material. When coupled with an independent measurement of coating thickness the coating density can be determined with a high precision. Conversely, if the density is known or assumed (e.g. literature value), the coating thickness can be established, non-destructively, with a precision of the order of 1%. Suitable combinations of measurement results allows the sensitivity to the uncertainty in each of the determined parameters in the set to be minimised. The adoption of an iterative approach can reduce the uncertainties for an individual test further. Case studies are presented on various methods of data combination for bulk materials and for thin coatings of titanium nitride on AISI 304 stainless steel and sub-micron thickness niobium on (100) silicon.

11:30 AM R12.9
Indentation of Graded Nanostructured Materials. In-Suk Choi, Ming Dao and Subra Suresh; Dept of Materials Science & Engineering, MIT, Cambridge, Massachusetts.

In recent years, experimental and computational studies have shown that controlled gradients in elastic properties of engineering materials can offer appealing possibilities for suppression of damage at contact surfaces in some tribological applications. In this work, we consider the particular situation of controlled gradients in plastic properties beneath the region of contact between an indenter and a nanostructured materials. The gradients are envisioned as arising from controlled variations in grain size from nanometer to micrometer length scales with no variations in elastic properties. Systematic and parametric studies of the effects of yield strength and strain hardening exponent on frictionless normal indentation are carried out to develop a general perspective on the potential benefits and drawbacks of plasticity gradients. Indentation experiments on electrodeposited Ni and a wrought aluminum alloy with gradients in grain size and precipitation, respectively, are also conducted so as to compare predictions with experimental observations.

11:45 AM R12.10
A Nanoindentation Study of Thermally-Grown-Oxide Films on Silicon. Fatih Helvaci and Junghyun Cho; Mechanical Engineering, SUNY Binghamton, Binghamton, New York.

We explore influences of the substrate on mechanical behavior of thin films using a depth-sensing indentation. For this purpose, nanoindentation has been performed on thermally grown oxide (TGO) films on the silicon substrate. In-situ AFM images of the indented surfaces are also exploited to highlight the structural evolution that often appears as 'abnormality' in the load-displacement curve. One primary goal of this study is to extract 'film-only' mechanical properties from the nanoindentation data by isolating the effects of the substrates. It is shown that the substrate effects on elastic modulus are more notable than those on hardness due to a wide-ranging elastic deformation beyond the plastically deformed region as well as a high elastic mismatch between the film and the substrate. In addition, an inverse analysis is proposed to estimate a thickness of thin films grown on substrates. We use the nanoindentation data and known mechanical properties of the substrate as input parameters for this analysis. Thin film thickness estimation by such an inverse method is then compared to the one obtained from experimental measurements via ellipsometry. Consequently, this study will provide a fundamental understanding in mechanical phenomena of thin films occurring ranging from nm to μm scales.