SYMPOSIUM Q

Fundamentals of Nanoindentation and Nanotribology II

November 27 – 30, 2000

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TUTORIAL

FT Q: MEASURING MECHANICAL PROPERTIES IN THE NANOMETER REGIME

Monday, November 27, 2000
1:00 p.m. - 5:00 p.m.
Room 309 (Hynes)

Recent progress in the understanding and application of materials with characteristic dimensions in the nanometer regime (e.g. thin films and patterned structures, nanocrystalline materials, modified surface regions, nanoscale composites, etc.) has generated a great deal of interest in measuring the mechanical properties of nanometer scale volumes of materials. A number of methods based on nanoindentation and atomic force microscopy have been developed in recent years that provide quantitative mechanical property measurements from volumes as small as some tens of nanometers in diameter, or qualitative mechanical property imaging with a resolution of some nanometers.

In this tutorial, the fundamental principles of nanoindentation and atomic force microscopy are reviewed, the state of the art in experimentation and in interpretation of data is described in some detail, and recent developments and achievements in this field are introduced. Instrumentation, data analysis models, and recent new knowledge obtained using these methods will be presented.

The tutorial should be of interest to graduate students and researchers who are entering this field, and to technologists or researchers who are concerned with mechanical properties at the nanometer scale.

Instructors:
Shefford P. Baker, Cornell University
Nancy Burnham, Worchester Polytechnic Institute

SESSION Q1: MODELING AND SIMULATIONS
Chair: Neville R. Moody
Tuesday Morning, November 28, 2000
Room 309 (Hynes)

8:30 AM *Q1.1
A SCALING APPROACH TO MODELING INDENTATION MEASUREMENTS. Yang-Tse Cheng, General Motors Research and Development Center, Warren, MI; Che-Min Cheng, Institute of Mechanics, Chinese Academy of Sciences, Beijing, CHINA; Zhiyong Li, Purdue University, West Lafayette, IN.

For over one hundred years, indentation experiments have been performed to obtain the hardness of materials. Recent years have seen significant improvements in indentation equipment and a growing need to measure the mechanical properties of materials on small scales. It is now possible to monitor, with high precision and accuracy, both the load and displacement of an indenter during indentation experiments. However, questions remain, including what properties can be measured using instrumented indentation techniques and what is hardness?
We discuss these basic questions using dimensional analysis and finite element calculations. We derive scaling relationships for loading and unloading curve, initial unloading slope, contact depth, and hardness. The relationship between hardness and the basic mechanical properties of solids, such as Young's modulus, initial yield strength, and work-hardening exponent, is then revealed. It is shown that the hardness value is not necessarily 3 times the yield strength value. The conditions for piling-up and sinking-in of surface profiles during indentation are obtained. The methods for estimating contact depth from initial unloading slope are evaluated. The work done during indentation is also studied. A relationship between hardness, elastic modulus, and the work of indentation is discovered. This relationship offers a new method for obtaining hardness and elastic modulus. In addition, we demonstrate that stress-strain relationships may not be uniquely determined from loading-unloading curves alone using a single conical or pyramidal indenter. The dependence of hardness on indenter geometry is also investigated. Finally, a scaling theory of indentation in power-law creep solids using self-similar indenters is developed. A connection between creep and indentation size effect is established.

9:00 AM Q1.2
FINITE ELEMENT MODELING OF NANOINDENTATION MEASUREMENTS OF CRYSTALLINE AND AMORPHOUS Si. J.A. Knapp, D.M. Follstaedt, G.A. Petersen and S.M. Myers, Sandia National Laboratories, Albuquerque, NM.

Finite-element modeling has proven to be a valuable tool for interpreting nanoindentation measurements obtained from samples such as thin films or ion-implanted layers, allowing the mechanical properties of the films to be separated from those of the underlying substrates. For the case of Si, the measurement is greatly complicated by pressure-induced phase changes and cracking. We have performed extensive indentation testing of both crystalline and self-ion-implanted, amorphous Si, on both bulk Si and Si-on-Insulator substrates. The residual indents were examined with atomic force microscopy (AFM) and both secondary (SEM) and transmission electron microscopy (TEM). Detailed finite-element simulations of the indentations were performed with the usual 2-dimensional axisymmetric approximation and with a full 3-dimensional description. By modeling the materials as isotropic, elastic-plastic solids with a Mises yield criteria, the amorphous Si is shown to have a yield strength and elastic modulus about 20% lower than crystalline Si. Furthermore, comparisons of the extent of cracking and deformation indicate that amorphous Si is more ductile and that it may not undergo phase changes during indentation. This talk will present the results of our measurements and calculations, including the those of ongoing examinations of the effects of phase changes using microscopy and detailed 3-dimensional finite-element simulations. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, supported by the US Department of Energy under contract DE-AC04-94AL85000. This work was supported through their Office of Basic Energy Sciences.

9:15 AM Q1.3
A FINITE ELEMENT STUDY ON THE NANOINDENTATION OF THIN FILMS. Xi Chen, Joost Vlassak, John W. Hutchinson, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA.

Nanoindentation is a technique commonly used for measuring thin film mechanical properties such as hardness and stiffness. Typically, shallow indentations with contact depths less than 10-20% of the film thickness are used to ensure that measurements are not affected by the presence of the substrate. In this study, we have used the finite element method to investigate the effect of substrate and pile-up on hardness and stiffness measurements of thin film systems. We find that: i) for soft films on hard substrates, the hardness is independent of the substrate as long as the indentation depth is less than 50% of the film thickness; ii) as soon as the hardness exceeds that of the substrate, the substrate effect becomes significant, even for indentations as shallow as 5% of the film thickness; iii) if the film is at least 20 times harder than the substrate, the plastic zone is mostly confined to the substrate while the film conforms to the deformed substrate by bending. We define a substrate influence factor and construct a map that may be useful in the interpretation of indentation measurements on thin films. The effect of the substrate on the pile-up behavior of thin films is discussed and contour plots of the plastic zone for various film/substrate property combinations are presented. The indentation moduli obtained from the finite element analysis are compared to the results from previous theoretical models for indentations in bulk material and thin films and a new technique for determining the contact area between indenter and material is suggested. The results obtained in this study are very useful when it is not possible to make indentations shallow enough to avoid the influence of the substrate on the measurements.

9:30 AM Q1.4
A NEW TECHNIQUE FOR CALCULATING THE HARDNESS AND MODULUS FROM INSTRUMENTED INDENTATION DATA. Warren C. Oliver, MTS Systems Corporation, Nano Instruments Innovation Center, Oak Ridge, TN.

The most generally accepted method for calculating the hardness and modulus using instrumented indentation data uses three experimentally determined parameters and a geometric description of the indenter. The three parameters used are the load on the indenter, the displacement of the indenter past the point of contact, and the slope of the unloading curve. The depth is first corrected for the elastic deflection of the surface, using the unloading slope, and then substituted into the geometric description of the indenter to yield the contact area. This contact area, together with the load, yields the hardness. Used together with the unloading slope, the modulus is obtained. This technique requires that the geometric description of the indenter be quite accurate. A new technique that uses the slope of the loading curve instead of the depth of indentation will be presented. This technique significantly reduces the sensitivity of the calculated hardness and modulus values to the geometric description of the indenter, particularly at shallow depths.

9:45 AM Q1.5
LOAD-DISPLACEMENT BEHAVIOR DURING SHARP INDENTATION OF ELASTO-VISCO-PLASTIC MATERIALS.

Robert F. Cook, Michelle Oyen-Tiesma, Yvete A. Toivola, University of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

A constitutive equation is developed for geometrically-similar sharp indentation of a material capable of elastic, viscous, and plastic deformation. The equation is based on a series of elements consisting of a quadratic (reversible) spring, a quadratic (time-dependent, reversible) dashpot, and a quadratic (time-independent, irreversible) slider-essentially modifying a model for an elastic-perfectly plastic material by incorporating a creeping component. Load-displacement solutions to the constitutive equation are obtained for both load-controlled and displacement-controlled indentation during constant loading- or displacement-rate testing, respectively. A characteristic of the former is the appearance of a forward-displacing "nose" during unloading of load-controlled systems (e.g., magnetic-coil-driven "nanoindentation" systems). Even in the absence of this nose, and the associated initial negative unloading tangent, load-displacement traces (and hence inferred modulus and hardness values) are significantly perturbed on the addition of the viscous component. A trivial extension of a conventional indentation procedure allows modulus, hardness, and viscosity to be deconvoluted from a three-step load-unload-reload contact sequence.

10:30 AM Q1.6
MOLECULAR DYNAMICS SIMULATIONS OF NANO-INDENTATION. Hualiang Yu, Arizona State University, Science and Engineering of Materials Program, Tempe, AZ; James Adams, Arizona State University, Dept of Chemical, Bio, and Materials Engineering, Tempe, AZ; Yang-Tse Cheng, General Motors Research and Development Center, Warren, MI; Louis Hector Jr, Surface Science Division, ALCOA Technical Center, ALCOA Center, PA.

A series of molecular dynamic simulations have been performed in order to study the nanoindentation of a hard pyramidal tip into an Al (100) surface. The effects of several variables are investigated, including temperature, tip-substrate bonding and indentation force. The indentation loading and unloading curves are generated during simulation and we compare it with experimental results. Also, we discuss the relationship between hardness and the indentation depth of Aluminum.

10:45 AM Q1.7
MOLECULAR DYNAMICS SIMULATIONS OF NANOINDENTATION OF SILICON NITRIDE - PLASTIC DEFORMATION AND MECHANICAL PROPERTIES. Phillip Walsh, Rajiv K. Kalia, Aiichiro Nakano and Priya Vashishta, Concurrent Computing Laboratory for Materials Simulation, Louisiana State University, Baton Rouge, LA; Subhash Saini, Numerical Aerospace Simulation Facility, Nasa-Ames Research Center, Moffett Field, CA.

10 million atom molecular dynamics simulations of crystalline and amorphous silicon nitride are performed using various indenter geometries. Mechanical properties such as hardness and elastic moduli are determined and compared with experiment. Local pressure distributions, images of atomic configurations, and local bond angle distributions are used to investigate mechanisms of plastic deformation in silicon nitride during nanoindentation. Local amorphization and fracture are observed in the region of the indent. Hardness of silicon nitride estimated from the simulations is within reasonable agreement with experiment.

SESSION Q2: SCANNING PROBE METHODS
Chair: Nancy A. Burnham
Tuesday Morning, November 28, 2000
Room 309 (Hynes)

11:00 AM *Q2.1
AN ATOMIC FORCE MICROSCOPY PERSPECTIVE ON MEASURING NANOMECHANICAL PROPERTIES. Richard Colton, Naval Research Laboratory, Surface Chemistry Branch, Washington, DC.

In 1986, Binnig, Quate and Gerber introduced the atomic force microscope (AFM) as a complementary tool to the scanning tunneling microscope (STM) capable of imaging the surface of insulators with high spatial resolution. Shortly after the invention of the AFM, two research groups realized other important applications of AFM in nanotribology and nanomechanics. In 1987, the IBM Almaden group-Mate, McClelland, Erlandsson and Chang-reported lateral force measurements showing "atomic" stick-slip phenomena on the surface of graphite. In 1989, the NRL group-Burnham and Colton-reported force-distance curves recording attractive, repulsive and adhesive interactions as a function of tip-surface separation. In time both of these AFM-based techniques have matured into quantitative probes of tribological processes, mechanical properties and adhesion at the nanometer scale. This paper will review some of the highlights and pitfalls leading to the development of these quantitative probes. With respect to development of AFM-based nanoindentation, two important techniques, namely, depth-sensing nanoindentation and force modulation, have been combined to form a new hybrid instrument capable of measuring the surface sensitive nanomecahnical properties-stiffness, modulus, hardness, damping losses and creep-of thin films and compliant materials.
Work done under ONR sponsorship and in collaboration with N. Burnham, S. Hues, C. Draper, D. Shafer, S. Corcoran, K. Wahl, and S.A. Syed Asif.

11:30 AM Q2.2
LATERAL FORCE MODULATION AND RHEOMETRICS STUDY ON THE CROSSLINK DYNAMICS OF ELASTOMERS.
Yimin Zhang, S. Ge, M. Rafailovich, J. Sokolov, Dept. of Mat. Sci. and Eng., SUNY at Stony Brook, NY; D. Peiffer, ExxonMobil Res. and Eng. Co., Annandale, NJ; J.A. Dias, K.O. McElrath, ExxonMobil Chem. Co., Baytown, TX; R.H. Colby, Penn. State Univ, Dept. of Mat. Sci. & Eng., University Park, PA.

The atomic force microscope in the lateral force modulation (LFM) mode has been used to characterize the surface modulus. The surface modulus is directly correlated with the surface crosslink density. Brominated poly(isobutylene-co-paramethylstyrene) (BIMS) is a synthetic terpolymer of isobutylene (IB), para-methylstyrene (PMS), and para-bromomethylstyrene (BrPMS). The mechanical properties can be controlled by varying the PMS content and the molecular weight, while the BrPMS content is varied to introduce chemical functionalities and chemical crosslinks. BIMS can be efficiently crosslinked by N, N′-Dicinnamylidene-1,6-Hexanediamine at 120°C. Using LFM, we studied the crosslink dynamics of several types of BIMS elastomers of different PMS and BrPMS content. LFM appears to be more sensitive to the surface modulus compared to other techniques such as friction force modulation. The result shows the rate of the crosslinking reaction at the surface is sensitively affected by the bromine content of the BIMS, the amount of crosslinker, and the reaction time. The result will be compared with measurements of the bulk modulus on the same samples.

11:45 AM Q2.3
THERMOMECHANICAL FORMATION AND THERMAL SENSING OF NANOMETER-SCALE INDENTATIONS IN PMMA THIN FILMS FOR PARALLEL AND DENSE AFM DATA STORAGE.
G. Cross, M. Despont, U. Drechsler, U. Dürig, W. Häberle, M.I. Lutwyche, H. Rothuizen, R. Stutz, R. Widmer, G.K. Binnig and P. Vettiger, IBM Research, Zurich Research Laboratory, Rüschlikon, SWITZERLAND; W.P. King and K.E. Goodson, Department of Mechanical Engineering, Stanford University, Stanford, CA.

Thermomechanical writing occurs as Joule-heated, cantilevered tips imprint nanometer-scale indentations (bits) in a 50-nm-thick polymer (PMMA) film. Thermal data reading incorporates the same cantilevers operated in a mode to detect a temperature change when a tip follows the contour of a previously written bit. Binnig et al. [1] demonstrated single-cantilever writing and reading density at 400 Gbit/in^2. A micromachined 32×32 cantilever array has been fabricated [2] and has demonstrated parallel read/write operation at 150 Gbit/in^2 [3]. Whereas much progress has been made to develop a thermomechanical data storage device [4], the fundamental process of thermomechanical bit formation is not well understood. Furthermore, macroscopic polymer rheological parameters are unlikely to apply as the bit size approaches the polymer molecule radius of gyration. We have performed detailed investigations of the thermomechanical storage processes for various cantilever designs by applying atomic force microscope (AFM) based force detection during thermal operation. We examine the thermomechanics of polymer indentation with respect to bit size, bit density, and write speed. Design tradeoffs of data reading signal-to-noise with operational bandwidth and power consumption are discussed and compared with a finite-difference model thermal and electrical simulation [5]. Also, we investigate issues of bit lifetime and wear-induced signal degradation through studies of the rheology of a confined viscoelastic medium. This work impacts the design of AFM cantilevers for combined thermal writing and reading as well as the understanding of fundamental polymer mesoscopic transport.
[1] G.K. Binnig et al., Appl. Phys. Lett. **74**, 1329-1331 (1999).
[2] M. Despont et al., Sensors & Actuators A **80**, 100-107 (2000).
[3] M.I. Lutwyche et al., submitted to Appl. Phys. Lett.
[4] P. Vettiger et al., IBM J. Res. Develop. **44**, 323-340 (2000).
[5] W.P. King et al., *Design of AFM Cantilevers for Combined Thermomechanical Data Writing and Reading*, Proc. Hilton Head 2000 Sensor and Actuator Workshop, 1-5 (2000).

SESSION Q3: NEW METHODS
Chairs: Oliver Kraft and David F. Bahr
Tuesday Afternoon, November 28, 2000
Room 309 (Hynes)

1:30 PM Q3.1
QUANTITATIVE STUDY OF NANOSCALE MECHANICAL PROPERTIES OF NANOSTRUCTURES. S.A. Syed Asif, Florida Univ, Department of Materials Science and Engineering, Gainesville, FL; K.J. Wahl, R.J. Colton, Code 6170, Surface Chemistry Branch, Naval Research Laboratory, Washington, DC.

Depth sensing nanoindentation and atomic force microscopy are widely used to study the nanoscale mechanical properties of materials. While both instruments can be used to determine materials properties at the nanoscale, each technique has distinct advantages and disadvantages. However, we find that coupling the AFM with depth-sensing indentation and AC force modulation can provide the best of both techniques. In this presentation we will discuss the application of force modulation to study the mechanical properties of nanostuctured materials - metallic nanowires 50 nm to 20 micron wide and 50 nm tall on a silicon substrate. We show that it is very difficult to measure the true response of nanowires using depth-sensing indentation alone. With force modulation we can detect the surface of the specimen, study the tip surface interaction and measure the true mechanical response of the material quantitatively below a length scale of 10 nm. We will also present the effect of constraint, local defect density, and surface condition on the nanoscale mechanical properties of materials and nanostructures.

1:45 PM Q3.2
SUB-MICROMETER SPATIALLY RESOLVED MEASUREMENTS OF MECHANICAL PROPERTIES AND CORRELATION TO MICROSTRUCTURE AND COMPOSITION. M. Kunert, University of Stuttgart, Stuttgart, GERMANY; B. Baretzky, E.J. Mittemeijer, Max Planck Institute for Metals Research, Stuttgart, GERMANY; S.P. Baker, Cornell University Department of Materials Science and Engineering, Ithaca, NY.

The microstructure of surface engineered materials can be very complex and may be inhomogeneous in both the vertical and the lateral directions. For example, if a Ti-6Al-4V alloy is implanted with carbon ions, a complex variation of microstructure with depthwhich is in addition to the existing two-phase structure of the alloyis generated. Large gradients in composition and defect concentration, as well as formation of titanium carbide can occur. As a result, pronounced changes of properties with depth within the implanted region are induced.
The variations of hardness and modulus, chemical composition, and microstructure within a carbon implanted region (about 350 nm thick) of a Ti-6Al-4V alloy were measured using nanoindentation, Auger electron spectroscopy, X-ray photoelectron spectroscopy, and transmission electron spectroscopy, respectively. Correlations between mechanical properties, composition, and microstructure were made with a spatial resolution of about ± 20 nm. The problems that may arise in measuring and correlating in-depth variations of such a complex material on this scale are outlined and a successful method is proposed. The need for, and the realization of, highly spatially resolved measurement techniques is emphasized.

2:00 PM *Q3.3
A METHOD FOR RESIDUAL STRESS MEASUREMENT BY NANOINDENTATION WITH SPHERICAL INDENTERS. George M. Pharr, J. Gregory Swadener, The University of Tennessee, Dept of Materials Science & Engr, Knoxville, TN, and Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN; Bostjan Taljat, STEEL Group, Treviso, ITALY and Faculty of Mechanical Engineering, University of Ljubljana, SLOVENIA.

Previous experimental studies and finite element simulations have shown that the measurement of residual stresses by nanoindentation methods with sharp Berkovich indenters is difficult. While residual stress affects the indentation load-displacement behavior, largely through changes in the pile-up geometry, the influence is not large enough to yield practical techniques for residual stress measurement. New experimental work coupled with finite element simulation is presented which shows that much larger effects are obtained with spherical indenters. A method for stress measurement is proposed and checked by experiments conducted in aluminum alloy specimens to which controlled levels of biaxial tension and compression could be applied. The method requires either an independent estimate of the material's yield strength, or a reference specimen of the material in a known state of stress, e.g., stress free.
Research at the Oak Ridge National Laboratory SHaRE User Facility was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

2:30 PM Q3.4
ON THE MEASUREMENT OF STRESS-STRAIN CURVES BY SPHERICAL INDENTATION. Erik G. Herbert, MTS Systems Corporation, Oak Ridge, TN; George M. Pharr, University of Tennessee, Knoxville, TN, and Oak Ridge National Laboratory, Oak Ridge, TN; Warren C. Oliver, MTS Systems Corporation, Oak Ridge, TN; Barry N. Lucas, Fast Forward Devices, LLC, Knoxville, TN.

It has been proposed that with the appropriate models, Instrumented Indentation Test (IIT) data can be reduced to yield the uniaxial stress-strain behavior of the test material. However, very little work has been done to directly compare the results from uniaxial tension and spherical indentation experiments. In this work, uniaxial tension, compression, and indentation experiments have been performed on the aluminum alloy 6061-T6. The purpose of these experiments was to specifically explore the accuracy with which the analytical models can be applied to IIT data to predict the uniaxial stress-strain behavior of the metal.

2:45 PM Q3.5
PREPARATION OF TUNGSTEN TIPS FOR NANOINDENTATION AND COMPARISON WITH DIAMOND ON SOFT MATERIALS. Jaime C. Grunlan, Lorraine F. Francis, William W. Gerberich, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Tungsten tips have been prepared for nanoindentation using an electrolytic technique originally used for field-ion microscopy. Tips with radii of curvature from 0.3 - 3 μm were prepared using 0.38 mm diameter tungsten wire and varying applied voltage and KOH solution concentration. The performance of tungsten tips prepared in this manner has been compared to that of commercially produced diamond tips with equivalent radii when indenting bulk polymers. Moduli of both glass ($T_g > 20°C$)) and rubbery ($T_g < 20°C$) polymers, measured using tungsten tips, are comparable but slightly lower than those obtained using an equivalent size diamond tip. Furthermore, comparison of pull-off forces between tip and sample suggest that the greater adhesion between diamond and polymer, relative to tungsten-polymer adhesion, may be a contributing factor to mechanical property differences when using a spherical tip approximation. Pull-off forces are twice as great in the diamond-polystyrene case, on the order of 10% of the polystyrene yield stress. When these same tungsten tips are used to indent higher modulus materials, such as single crystal aluminum, large compliances and tip deformation are observed. The calculated result yields Young's moduli that are 50 - 70% of the expected 70 GPa that is obtained when diamond is used.

3:30 PM Q3.6
DETERMINATION OF THE REAL INDENTER SHAPE FOR NANOINDENTATION/NANOTRIBOLOGY TESTS BY SURFACE METROLOGICAL AND ANALYTICAL INVESTIGATIONS. Susan Enders, Howard Hawthorne, NRC Innovation Centre, Vancouver, CANADA; Peter Grau, M.-Luther Univ, Dept of Physics, Halle, GERMANY.

In contact experiments under high local loading knowledge of the shape and the expansion of the developing stress field is vitally important for the exact determination and proper interpretation of the mechanical properties of the material under study. To deduce the properties from the stress field it is thus necessary to know the actual shape of the indenter used. We make the assumption that as more tests are made, the indenter will not be evenly abraded and this infringes the indenter self-similarity needed for analysis. This happens not only during scratching experiments but also for the indentation test when uneven wearout can be recorded. In this paper a critical comparison of different kinds of surface metrological and profilometrical methods is made, as well as analytical investigations, to qualify the real indenter shape function. The surface mapping of indenter shapes was done by atomic force microscopy (AFM), scanning electron microscopy (SEM) and optical interferometric profilometry on actual indenters as well as on their indentations in soft materials. The different surface metrology systems allow a very precise estimation of the aberrations inherent in each method. To compare analytical calculations for determining area functions of indenters, their validity was surveyed on results of indentation tests made on standard calibration materials such as fused silica, sheet glass and isotropic single crystals. As an example, calculations based on both Hertz and Sneddon theories of pure elastic contact are thoroughly discussed. Together with various transition functions, these theories then yield the complete area function. The results obtained show the advantages and disadvantages of the respective theories by describing a rounded indenter tip. These investigations should help to avoid inaccurate material property evaluations due to incorrect determination of the real indenter shape.

3:45 PM Q3.7
3D FIB MAPPING OF NANOINDENTATION DEFORMATION ZONES. Timothy Steer, Günter Möbus, Beverley Inkson, Dept of Materials, University of Oxford, Oxford, UNITED KINGDOM; Oliver Kraft, Thomas Wagner, Max-Plank-Institut für Metallforschung, Stuttgart, GERMANY.

A novel technique has been developed to examine site-specific, subsurface microstructures in three dimensions (3D). A 3D data set is collected by successive cross-sectional slicing using a gallium focussed ion beam (FIB) and imaging using secondary electrons, enabling a 3D microstructure map to be generated using computer-based reconstruction techniques. In the first instance, this 3D FIB mapping technique has been applied to copper-based epitaxial metal multilayer coatings which have been deformed by nanoindentation. Profiles of the deformed subsurface interfaces have been generated in 3D. These individual interface maps allow analysis of the deformation in terms of both the thickness of individual layers and that of the entire film. Material flow, which is seen as pile-up and sink-in zones around the indent, can thus be precisely characterised. The site at which the sectioning is to be carried out can be chosen with high spatial resolution; consequently, nanoscale mechanical properties can be linked directly with an area's microstructure. In the case of the multilayer systems, particular indents were analysed and their deformation characteristics related to the specific hardness and moduli values which were measured during indentation. Since this 3D FIB mapping approach is not limited to the study of interfaces in coatings or deformation caused by nanoindentation, and could be applied to any material with subsurface structure of interest, it provides a unique and exciting insight into site-specific, subsurface microstructure.

4:00 PM Q3.8
DEVELOPMENT OF A NANOINDENTER FOR IN-SITU TRANSMISSION ELECTRON MICROSCOPY. E.A. Stach, D.K. Owen, T.T. Freeman, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; M.A. Wall, Materials Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA; A.M. Minor, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA; T. Chraska and R. Hull, Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA.

Nanoindentation has become one of the primary testing techniques used to determine the mechanical properties of thin films and small material volumes. In this technique, a sharp indenter of known geometry is forced into a material surface along a controlled orientation, and the displacement of the material is measured as a function of time. Using this load - displacement measurement one can determine the value of certain mechanical properties as well as infer the microstructural response. We have constructed a nanoindenter that resides within a transmission electron microscopy sample holder. This permits real time TEM observation of the microstructural responses of a material during nanoindentation. We will present results that include fracture of brittle materials (silicon), the indentation response of amorphous germanium, and dislocation motion and yielding in aluminum. The design of the piezoelectrically driven indentation holder will be discussed in detail. Additionally, our present development of a heated indenter tip and a heated sample will be delineated, as well as our scheme for the incorporation of a load measurement device. A critical issue in these in-situ experiments is the TEM sample geometry. While the use of focused ion beam lithography (FIB) allows relatively fast and simple sample preparation, the resulting electron transparent membranes bend relatively easily, introducing undesirable artifacts in some experimental observations of indentation. Our development of photolithographically prepared silicon mesas will be presented. This method yields controlled, reproducible samples with reduced experimental artifacts. Our results show that this in-situ technique allows direct, real time observation of the nanomechanical responses to indentation across a wide range of materials.

4:15 PM Q3.9
EXPERIMENTAL CONTACT MECHANICS STUDIES IN THREE DIMENSIONS. Barry N. Lucas, Jack C. Hay, Fast Forward Devices, LLC, Knoxville, TN; and Warren C. Oliver, MTS Systems Corporation, Oak Ridge, TN.

Mechanical and tribological properties at the nanometer-scale are of vital importance to a number of U.S. industries. This is evidenced by the broad range of applications where an adherent, hard, thin, wear-resistant coating plays an essential role in performance of a product or device. In an effort to continue the advancement of techniques available for mechanical characterization of surfaces, a new testing system has been developed that allows independent and dynamic control of the forces on, and the displacements of, a point probe in three dimensions. This capability not only allows studies of dynamic frictional properties during the initial stages of contact between the probe and a surface, but also the investigation of the three-dimensional elastic response of the surface as the direction of the strain vector into the surface is systematically varied. The initial observations and results from this new system when applied to a number of surfaces will be presented and discussed.

4:30 PM Q3.10
LOAD-DISPLACEMENT BEHAVIOR DURING MACRO-INDENTATION. Yvete A. Toivola, Matthew L. Cunningham, Dylan J. Morris, Robert F. Cook, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN.

Load and displacement measurement during indentation provides a means of estimating material modulus and hardness values without direct observation of the indentation contact impression. Such measurements are thus extremely useful for evaluating material properties on extremely small scales at which it is difficult or impossible to observe the contact impression or in which the measurement is constrained to small volumes (e.g., in thin films). Hence, "nanoindentation" techniques have been developed, focusing on deconvoluting load-displacement indentation traces to obtain underlying material properties. In this talk, the design and usage of a macroindenter is described. The instrument allows load and displacement to be measured during indentation events at length and load scales (up to 100 N) at which instrumentation and probe-geometry calibration difficulties systemic to nanoindentation are avoided. In addition, the instrument provides the capability for direct observation of contact, thereby allowing contact area and fracture and delamination events to be tracked during simultaneous load-displacement measurement. Load-displacement results for a variety of monolithic materials and film-on-substrate systems are presented and interpreted in terms of conventional modulus-hardness deconvolution procedures. It is suggested that macroscopic measurements, in which there are few instrumentation difficulties, might provide a better vehicle for assessing indentation contact models.

4:45 PM Q3.11
SUB-MICRON INDENTATION AT VERY HIGH TEMPERATURES. Trevor Bell, Alexander Bendeli, Leszek Wielunski, Anthony Fischer-Cripps, CSIRO Telecommunications and Industrial Physics, Sydney AUSTRALIA; Mark Hoffman, University of NSW, AUSTRALIA.

A critical aspect of understanding wear behaviour of materials is the determination of the mechanical properties of the materials at temperatures corresponding to those resulting from friction and/or in-service environmental conditions. Sub-micron indentation testing can be used to determine mechanical properties of materials at the same microstructural level at which wear mechanisms operate. A high-temperature indentation testing instrument, capable of measuring indentation force and displacement at high resolution on samples in situ up to temperatures of 1100°C, has been developed. The device is also suitable for analysing a wide range of mechanical properties including, for example, those of thermal barrier coatings and electronic components at elevated temperatures. The present work gives details of the instrument and preliminary results obtained on a series of metal-ceramics composites.

SESSION Q4: DEFORMATION AND DEFORMATION MECHANISMS I
Chairs: Donald E. Kramer and Eric A. Stach
Wednesday Morning, November 29, 2000
Room 309 (Hynes)

8:30 AM *Q4.1
CHARACTERISING THE PROPERTIES OF VERY THIN (<200 nm) COATINGS BY LOW LOAD NANOINDENTATION TECHNIQUES: THE BENEFITS OF USING BOTH 'SHARP' AND 'BLUNT' INDENTERS. T.F. Page, E.G. Berasategui, I. Arce-Garcia, N. Tymiak[a] and S.J. Bull, Materials Division, University of Newcastle, Newcastle upon Tyne, UNITED KINGDOM. [a]Department of Chemical Engineering & Materials Science, University of Minnesota, MN.

We are exploring the use of very low load continuously-recording indentation techniques (eg. >5mN with a Nanoindenter II and >1mN with a Hysitron/Park AFM) to measure the properties of thin costings (<200 nm thick) on both glass and silicon. The coatings comprise a number of monolithic and multi-layer CVD and sol-gel materials on glass and magnetron/sputtered & -beam evaporated carbon nitride on silicon. Both sharp (<50 nm tip-end radius) and 'blunter' (~200 nm tip-end radius) indenters have been used. Indentation with sharper tips produces well-behaved load-displacement curves from which all the expected quantitative data regarding plastic and elastic work, hardness and modulus values (and their variation with indenter displacement) can be calculated and thus the changes in properties conferred on the substrates by the coatings quantitatively measured. We have even been able to mechanically detect the difference between the two sides of commercial float glass! The blunter indenter provides complementary information in that it is possible to use Hertzian mechanics to detect the onset of plastic flow and the load displacement curves in these cases often show much clearer evidence for the existence of soft surface layers, coating debonding and coating buckling (under the action of residual stresses).

9:00 AM Q4.2
FILM FRACTURE CONTROLLED EXCURSIONS IN OXIDE - METAL SYSTEMS. D.F. Bahr, M. Pang, and D. Rodriguez-Marek, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Discontinuities during both load and depth controlled continuous indentation tests have been ascribed to dislocation nucleation or multiplication and film fracture. In the case of materials with low dislocation densities, such as annealed single crystals of iron, tungsten, and GaAs, it is very difficult to determine which event is controlling the excursion. In most of these cases, the excursion has been attributed to dislocation nucleation and multiplication, and any subsequent film fracture is merely a result of the large strains which occur on the surface of the sample during the excursion. However, in materials which exhibit permanent deformation prior to a discontinuity in loading, it is more likely that the phenomena is indeed controlled by film fracture, and not the rapid generation of dislocations. The current study has been undertaken to examine the properties of passivating films on engineering alloys as well as model systems of single crystal iron and aluminum. An electrochemical cell coupled with a scanning probe microscope and nanoindentation system allows growth of passive films on an austenitic stainless steel as well as a titanium alloy. The occurrence of excursions is shown in these materials to be linked directly with film fracture, rather than dislocation multiplication. A complementary set of ex situ experiments shows the presence of deformation prior to film fracture with both load - depth sensing techniques as well as imaging the surface topography.

9:15 AM Q4.3
INDENTATION OF THIN-FILM COATINGS ON SUBSTRATES: EXPERIMENTS AND ANALYSIS. M. Dao, K. Van Vliet, S. Suresh, Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

The analysis of the mechanics of indentation in thin metal films is complicated by the effect of the underlying substrate on the elastoplastic deformation of the film. In this paper, we present a combined experimental and computational approach for coated film/substrate systems to address the following fundamental issues: 1) the range of film thicknesses for different film/substrate combinations for which continuum elastoplastic models adequately describe the indentation response, 2) the geometric conditions and material properties for which the substrate strongly influences the deformation of the film, and 3) the effect of residual stress in the film on indentation response. Thin films of aluminum on brittle substrates as well as bulk aluminum diffusion-bonded to brittle substrates are subjected to depth-sensing nano-, micro- and macro-indentation. The ensuing indentation responses are quantitatively assessed by comparisons with the predictions of two-dimensional as well as full three-dimensional finite element results. The validity and limitations of continuum mechanics-based models (including physically based crystal plasticity models) and the conditions governing the onset of discrete deformation modes are discussed.

9:30 AM Q4.4
ARGON IRRADIATION AND ANNEALING TEMPERATURE EFFECTS ON POP IN EVENTS DURING NANOINDENTATION OF POLYCRISTALLINE IRON. Carlos M. Lepienski, Andreia C. Tavares, Neide K. Kuromoto, Dept. Fisica, Univ. Fed. do Paraná, BRAZIL; Carlos E. Foerster, Francisco C. Serbena, Dept. Fisica, Univ. Est. de Ponta Grossa, BRAZIL.

The indentation of metallic materials shows considerably complexity. At small depths, nanoindentation loading curves in single crystals shows pop in events which are commonly indicated as yield point loads. We investigated the effect of annealing temperatures and argon irradiation on the occurrence of pop in polycrystalline iron (Fe 99.99%) during nanoindentation. Samples of iron were mechanically polished with abrasive processes finishing using diamond powder with diameter of 0.25 μm. After polishing the samples were annealed at 700°C by 20 min, and then the temperature was decreased at a low rate to room temperature. After annealing pop in events were observed at almost all loading curves. Annealed samples were then mechanically polished again with alumina powder (1μm diameter) and diamond powder (0.25μm). Pop in events were not observed in nanoindentation after second polishing process. Other annealed samples were irradiated with argon ions at 240keV. Pop in events are still present in the loading curves in these samples even after irradiation. The mechanically polished samples were then submitted to annealing at temperatures from 300°C to 700°C, at intervals of 100°C and nanoindentation tests were performed after each annealing. The pop in event frequency increases with annealing temperature. These results are discussed in terms of defects generated by mechanical polishing and argon ion irradiation.

9:45 AM Q4.5
DETERMINATION OF MATERIAL PROPERTIES OF POLYMERIC MATERIALS THROUGH NANOINDENTATION TESTS AND FINITE ELEMENT MODELING. Byung Ro Kim, Timothy C. Ovaert, The Pennsylvania State University, Dept of Mechanical and Nuclear Engineering, University Park, PA.

Nanoindentation techniques are utilized extensively to characterize a wide variety of thin coatings, both hard and soft. In this study, a four-parameter axisymmetric visco-elastic/plastic finite element model, a simplified model of five parameter model proposed earlier, has been suggested to explain the behavior of polymer coatings subject to nanoindentation tests utilizing 1 micron radius spherical indenters. The four parameters in modified Kelvin-voigt model account for both visco-elastic and plastic response in the coating, and are determined by a process that matches the experimental load versus indentation depth plot from the test with that from the finite element model. The model not only provides more useful information than an ordinary method using unloading curve or sinusoidal load but also has an advantage of less iteration time when compared to five-parameter model.

10:30 AM *Q4.6
NANOMECHANICS OF PLASTIC DEFORMATION DURING INDENTATION. Subra Suresh, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

This presentation will deal with recent experimental and theoretical studies of the nanomechanics and micromechanics of elastoplastic deformation in metals subjected to indentation. Particular attention will be devoted to the identification of the transitions from continuous deformation processes to discrete deformation micromechanisms as the size scales are reduced from microindentation to nanoindentation. Experimental studies of indentation will be supplemented with transmission and scanning electron microscopy and atomic force microscopy in an attempt to probe the nanomechanisms of indentation. The effects of grain boundaries, crystallographic texture, surface roughness, initial defect density, and defect nucleation and mobility on the nanoindentation response of a variety of metallic materials will be considered. Conceptual and quantitative models will be presented to rationalize the experimentally observed nanomechanistic processes.

11:00 AM Q4.7
INDENTATION OF AN ALUMINUM THIN FILM ON A GLASS SUBSTRATE: EXPERIMENTAL AND MECHANISM-BASED STRAIN GRADIENT PLASTICITY STUDIES. R. Saha, Stanford Univ, Dept of Materials Science and Engineering, Palo Alto, CA; Z. Xue, Univ of Illinois, Dept of Mechanical Engineering, Urbana, IL; W.D. Nix, Stanford Univ, Dept of Materials Science and Engineering, Palo Alto, CA; Y. Huang, Univ of Illinois, Dept of Mechanical Engineering, Urbana, IL.

Micro-indentation hardness test is a reliable experimental method to determine the mechanical properties at the microscale. We present an experimental study of micro-indentation hardness test of an aluminum thin film on a glass substrate. The experiments clearly display very strong size effects for small depth of indentation ($\ll$ film thickness) as well as for large depth of indentation (close to film thickness). We have used the theory of mechanism-based strain gradient (MSG) plasticity to study micro-indentation experiments for the Al film/glass substrate system. It is established that the MSG plasticity theory captures the observed size effect very well, while classical plasticity theories clearly fall short for small and large depths of indentation.

11:15 AM Q4.8
YIELDING AND THE INDENTATION SIZE EFFECT IN IRIDIUM. J.G. Swadener, E.P. George and G.M. Pharr, Oak Ridge National Laboatory, Metals and Ceramics Division, Oak Ridge, TN; University of Tennessee, Dept. of Materials Science and Engineering.

Iridium alloys have several properties that make them excellent model materials in nanoindentation studies. They have high resistance to oxidation, a large elastic modulus (560 GPa), and a relatively low yield strength (160 MPa for Ir-0.3 pct W). From nanoindentation experiments with a 69 micron radius spherical indenter, the yield

strength of Ir-0.3 pct W was determined to be 2.9 GPa. This value is 18 times the yield stregth of the bulk material, but still much lower than the shear modulus (225 GPa) or the theoretical yield strength of the material. The large yield stress for the 69 micron spherical indenter appears to be due to the indentation size effect. The effect will be further assessed by using spherical indenters with larger radii. Nanoindentation experiments with a Berkovich indenter show a large indentation size effect, which extends to much greater depths in iridium than in most materials. For a Berkovich indenter, hardness values range from 3.1 GPa at a contact depth of 2.7 microns to 5.9 GPa at a contact depth of 0.37 microns. In iridium alloys, the indentatio size effect appears to extend through the microhardness regime and possibly into the macrohardness regime.
Research at the Oak Ridge National Laboratory SHaRE User Facility was sponsored by the division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

11:30 AM Q4.9
NANOINDENTATION OF SINGLE AND POLYCRYSTALLINE FCC METALS. Andrew Gouldstone, Krystyn Van Vliet, Subra Suresh, Massachusetts Institute of Technology, Dept of MS&E, Cambridge, MA.

Nanoindentation experiments were performed on a variety of single crystal FCC metals, in both thin film and bulk form and of different crystallographic orientation and vastly differing elastic properties. In addition, nanoindentation was conducted on polycrystalline FCC metal thin films with different grain sizes and known crystallographic texture. Deformation under the nanoindenter was studied by recourse to continuous depth-sensing indentation where the indentation load was recorded as a function of depth of penetration. The elastic and plastic portion of deformation under the indenter, along with regions of discrete and continuous plastic deformation, were documented for all these experimental conditions. The role of dislocation nucleation and motion during nanoindentation in facilitating discrete displacement bursts was analyzed by invoking an energetics model. In addition, a bubble raft model was constructed and tested as a visual tool in interpreting the nucleation and motion of dislocations during nanoindentation. The effects of film thickness, grain size, texture and the presence of pre-existing defects in the films on the indentation response were analyzed. The effect of these variables on the onset of discontinuous plastic deformation was also examined.

11:45 AM Q4.10
PROBING THE CRITICAL STRESS INTENSITY FACTOR FOR SLIP TRANSFER OF GRAIN BOUNDARIES BY NANO-INDENTATION WITH AN AFM. Alfonso H.W. Ngan, The University of Hong Kong, Department of Mechanical Engineering, Hong Kong, PR CHINA.

Based on the concept of dislocation pile-up, a plasticity model has been developed to predict the variation of hardness with grain size and indent size for sub-granular indentation. The predicted relation has a $1/\sqrt{\text{grain size}}$ term resembling the Hall-Petch relation, and an additional log(grain size/indent size) term representing the relative importance of the pile-up zone to the total deformation volume. A further parameter assumed in the model and appearing in the predicted relation is the critical stress intensity factor for slip transmission across the grain boundary. This parameter is analogous to the Hall-Petch slope in uniaxial testing of polycrystalline specimens, but unlike the latter which is a global average, it is specific to the grain boundary of a single grain.
Two types of experiments have been used to check the validity of this relation. The first type of experiments is microhardness measurement on bicrystals and coarse-grained polycrystals. In these experiments, the distance of the indent from the grain boundary is taken as the "grain size", and plotting the hardness variation according to the form predicted by the present model shows good agreement with the model. The second type of experiments is micro- or nano- indentation on fine-grained polycrystals. Here, the grain size is fixed but the indentation size varies. These data also show qualitative agreement with the predicted relation.
In carrying out the nanoindentation experiments on fine-grained polycrystals, we have used a Hysitron® nanoindenter mounted on a Triboscope® scanning probe microscope. In such a set-up, the same tip is used for both nanoindentation and AFM imaging, so that one can do both imaging and indentation on the same platform. This technique is vital in the current exercise as it enables one to locate precisely the area to be indented, namely, the centre of a selected grain.

SESSION Q5: DEFORMATION AND DEFORMATION MECHANISMS II
Chair: Barry N. Lucas
Wednesday Afternoon, November 29, 2000
Room 309 (Hynes)

1:30 PM Q5.1
DEFORMATION BEHAVIOR OF THIN METAL FILMS INVESTIGATED BY NANOINDENTATION, MICROBEAM DEFLECTION AND FINITE ELEMENT CALCULATIONS. R. Schwaiger and O. Kraft Max-Planck-Institut für Metallforschung and Institut für Metallkunde, Universität Stuttgart, Stuttgart, GERMANY.

It is well known that the mechanical strength of polycrystalline thin metal films depends on the film thickness and on microstructural parameters such as the grain size. In general, the plastic behavior of thin film materials can be studied by tensile testing or possibly microbeam deflection giving results for yield stress and hardening rate. However, both techniques require a rather complicated sample preparation compared to nanoindentation. In this study, the deformation behavior of sputter-deposited Cu films with thicknesses between 0.3 and 1.5 μm is compared using nanoindentation and microbeam deflection. The films are deposited on micromachined silicon oxide cantilever beams (20 μm wide and 50 μm long). The beams were deflected using a nanoindentation system recording the load-displacement curves. Nanoindentation experiments on the same films were performed in regions of the sample where the film is supported by the substrate. The load-displacement curves obtained in both experiments are compared to results of finite element calculations. From this comparison, the yield stress and the work-hardening rate, assuming a bi-linear stress-strain behavior, were determined. In the microbeam experiments, the yield stress was found to increase with decreasing film thickness, while the work-hardening seems not to be significantly affected. The results from the indentation experiments followed the same trend of increasing yield stress with decreasing film thickness. However, it was not possible to fit the experimental data of both experiments with the same constitutive material's law. This might be due to the fact that the average strain during an indentation experiment is much larger than in the case of microbeam deflection experiments where the maximum strain is only about 1.5%. In summary, the use of a simple bi-linear material law is apparently not sufficient to describe the deformation behavior of thin films over a wide range of plastic strains.

1:45 PM Q5.2
DISLOCATION CONFIGURATIONS AROUND NANOINDENTATIONS IN RECONSTRUCTED Au(001). O. Rodríguez de la Fuente, M.A. González, J.M. Rojo, Dpto. de Física de Materiales, Universidad Complutense, Madrid, SPAIN.

The study of defect structures around indentations is a subject of much current interest[1] in view of its implication in the mechanical properties of solid surfaces. In this communication we report a Scanning Tunnel Microscopy (STM) study of nanoindentations resulting from STM tungsten tip contacts with the 5×20 reconstructed surface of a Au(001) crystal. Craters of rectangular shape, several interatomic distances deep, with sides about 10 nm long parallel to the compact <110> directions in the (001) face, are observed around the indentation points. Around these craters, a novel defect structure is recognized: it consists of rows of hillocks extending along more than a hundred nm along the <110> directions. These hillocks, about 7 nm of side and 0.06 nm in height, appear aligned in rows which look as double branches stemming from the craters. This spatial distribution can be described as dislocation rosettes, similar to the ones that are well known to arise around macroscopic indentations but reduced by a scale factor of about 10^4. With the help of simulation models we identify individual hillocks as dislocation configurations consisting of an unfaulted dislocation loop with Burgers vector parallel to the surface, which splits into two Shockley partials linked by a stair-rod segment that holds the two stacking-fault ribbons. Similar configurations have been previously recognized in Au(001)[2]. An interpretation of the hillocks spatial distribution in terms of the corresponding dislocation parameters (Burgers vector, dislocation direction, distance between dislocations, etc.) is proposed. [1] C.L. Kelchner, S.J. Plimpton, J.C. Hamilton, Phys. Rev. B 58, 11085 (1998); J.D. Kiely, R.Q. Hwang, J.E. Houston, Phys. Rev. Lett. 81, 4424 (1998). [2] J. de la Figuera *et al*, Phys. Rev. B 58, 1169 (1998).

2:00 PM Q5.3
MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ELECTROPLATED Cu THIN FILMS. A.A. Volinsky[1], J. Vella[2], I.S. Adhihetty[2], V. Sarihan[2], L. Mercado[2], B.H. Yeung[2] and W.W. Gerberich[1]. [1]University of Minnesota, Dept. of Chem. Engineering and Materials Science, Minneapolis, MN. [2]Motorola, Digital DNA Labs, Semiconductor Product Sector, AZ.

Copper films of different thicknesses of 0.2, 0.5, 1 and 2 microns were electroplated on top of the adhesion-promoting seed layers on < 100 > single crystal silicon wafers. Films were annealed in vacuum in order to enhance Cu grain growth. Cu films microstructures was characterized using Atomic Force Microscopy and Focused Ion Beam

Microscopy. Elastic modulus of 110 to 130 GPa and hardness of 1 to 1.6 GPa were measured using the continuous stiffness option (CSM) of the Nanoindenter XP. Thicker films appeared to be softer in terms of the lower modulus and hardness, exhibiting a classical Hall-Petch relationship between the yield stress and grain size. Lower elastic modulus of thicker films is due to the higher porosity and partially due to the surface roughness. Comparison between the mechanical properties of films on the substrates obtained by nanoindentation and tensile tests of the freestanding Cu films is made.

2:15 PM Q5.4
X-RAY MICROBEAM INVESTIGATION OF THE DEFORMATION MICROSTRUCTURE UNDER COPPER NANOINDENTS. W. Yang, B.C. Larson, G.E. Ice, J.Z. Tischler, J.D. Budai, K.-S. Chung, Oak Ridge National Lab.; G.W. Pharr, Univ. of Tennessee/ORNL; N. Tamura, Lawrence Berkeley National Lab.; and W.L. Lowe, Howard Univ.

High resolution x-ray microbeam measurements have been used to investigate the 3-dimensional deformation microstructure near nanoindents in single-crystal Cu. Broad band-pass (white) synchrotron x-ray microbeams of ~0.7 x 0.7 μm^2 cross-section were produced using elliptically figured Kirkpatrick-Baez mirrors on the MHATT-CAT beamline at the Advanced Photon Source. These beams have been used in connection with a CCD detector, interactive Laue diffraction software, and a newly developed technique for obtaining micron resolution along the penetration depth (~25 μm) to probe lattice rotations as a function of depth and position under Berkovitch nanoindents in $< 111 >$ oriented Cu. Nearly one-dimensional tilts of up to ~3 degrees were found below and extending beyond the flat faces of the indenter, while a much more complicated distribution of tilts with compound lattice rotations was observed below the tip and the sharp blades of the indenter. The x-ray microbeam methods for performing the measurements and data analysis will be discussed, and the outlook for detailed investigations of the fundamental aspects of materials deformation by combining nanoindentation techniques with 3-D x-ray microbeam measurements will be considered.
Research sponsored by the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725: the operation of the APS is sponsored by the DOE.

2:30 PM Q5.5
MECHANICAL PROPERTIES OF AS-GROWN AND ION-BEAM-MODIFIED GaN FILMS. S.O. Kucheyev, J.E. Bradby, J.S. Williams, C. Jagadish, The Australian National Univ, Dept of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Canberra, AUSTRALIA; M. Toth, M.R. Phillips, University of Technology, Sydney, Microstructural Analysis Unit, AUSTRALIA; M.V. Swain, The University of Sydney, Department of Mechanical and Mechatronic Engineering, AUSTRALIA.

The deformation behavior of wurtzite GaN films grown on sapphire substrates is studied by nanoindentation with spherical indenters. Atomic force microscopy (AFM) and cathodoluminescence are used to characterize the deformation mode. Slip is identified as one of the physical mechanisms responsible for the "pop-in" events observed during loading of as-grown crystalline GaN. Indentation with a ~ 4.2 μm radius spherical indenter at a maximum load up to 900 mN does not produce any cracking visible by AFM in as-grown GaN. Instead, under such loads, indentation results in a pronounced elevation of the material around the impression. Implantation disorder significantly changes the deformation behavior of GaN. In particular, we discuss the mechanical properties of (i) GaN films amorphized by ion bombardment and (ii) GaN films with a high concentration of implantation-produced planar defects.

SESSION Q6: ADHESION
Chair: William W. Gerberich
Wednesday Afternoon, November 29, 2000
Room 309 (Hynes)

3:15 PM Q6.1
QUANTIFICATION OF POST-CMP COPPER ADHESION TO AMORPHOUS SiN PASSIVATION VIA NANOINDENTATION. J.B. Vella, A.A. Volinsky, I.S. Adhihetty, Motorola, DigitalDNA Laboratories, MSL, Mesa, AZ; S.M. Smith, Motorola Labs, PSRL, Tempe, AZ.

Nanoindentation has been used to quantify the practical work of adhesion of oxidized post-CMP copper surface to SiN passivation. Poor adhesion of electrodeposited copper to SiN passivation is observed following CMP due to copper oxide growth prior to plasma enhanced silican nitride deposition. Four point bend testing has shown that failure of test structures occur at the Cu/CuO interface. Hydrogen and ammonia plasma treatments of the post-CMP copper surface are employed to not only remove the oxide but to increase the surface roughness of copper. Copper oxide reduction is shown by auger electron spectroscopy. Surface roughening of copper is shown by atomic force microscopy. Both effects are shown to increase the adhesion strength of the Cu/SiN interface by quantifying the practical work of adhesion of all samples via nanoindentation. Nanoindentation with a one-micron conical indenter was used to induce SiN film delaminations and correlate them to the practical work of adhesion [1]. In order to more reliably and repeatably produce these delaminations a TiW (10%Ti) superlayer was sputter deposited on to the test structures [2,3]. Mechanical properties, including elastic modulus and hardness of SiN, electrodeposited copper, and TiW were measured by nanoindentation. 1. D.B. Marshall, A.G. Evans, J. Appl. Phys., 56(10), 2632-2638, 1984. 2. M.D. Kriese, W.W. Gerberich, N.R. Moody, J. Mater. Res., 14(7), 3007-3018, 1998. 3. A.A. Volinsky, N.I. Tymiak, M.D. Kriese, W.W. Gerberich and J.W. Hutchinson, Mater. Res. Soc. Proc., 539, pp. 277-290, 1999.

3:30 PM Q6.2
DETECTION OF DISCRETE BONDS UPON RUPTURE OF MICROCONTACTS TO SELF-ASSEMBLED MONOLAYERS. Hjalti Skulason, C. Daniel Frisbie, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN.

Pull-off forces were measured under salt for Au coated atomic force microscopy (AFM) tips in contact with self-assembled monolayers (SAMs) bearing S-containing end groups known to bind to Au. In these experiments, the tip-SAM microcontacts involve approximately 100 molecules. The mean pull-off force required to break the Au-SAM microcontacts was seven times greater than with control SAMs having no S-containing groups. Further, rupture force histograms for the Au/S-containing SAM microcontacts showed 0.1 nN periodicity. We have assigned this 0.1 nN force quantum to rupture of individual chemical bonds and have estimated the bond energy to be on the order of 10 kJ/mol. The specific interaction corresponding to this energy appears to be abstraction of Au atoms from the tip surface upon pull-off. Force quanta were also observed in other microcontact experiments involving chemically modified tips and SAMs. Our ability to detect force quanta is a function of the solvent. In order to observe single bond rupture forces directly, the tip-substrate interfacial energy must be negative and larger in absolute value than the substrate-solvent and tip-solvent interfacial energies. Otherwise, non-specific solvent exclusion effects dominate the microcontact adhesion. These measurements demonstrate that pull-off forces can be sensitive to fluctuations in the number of discrete chemical interactions.

3:45 PM Q6.3
ADHESIVE FAILURE OF THIN EPOXY FILMS ON ALUMINIZED SUBSTRATES. N.R. Moody, Sandia National Laboratories, Livermore, CA; D.F. Bahr, Washington State University, Pullman, WA; M.S. Kent, J.A. Emerson, E.D. Reedy, Jr., Sandia National Laboratories, Albuquerque, NM.

Composition and structure are two of the most important factors controlling performance and reliability of thin film components. They are particularly important in components with thin polymer films where changes in composition and structure during processing and service can lead to interfacial failure. However, our understanding of interfacial failure in these systems is limited by the lack of established thin polymer film test techniques. We have therefore begun a program to determine the properties and adhesion of Epon 828/T403 using nanoindentation and stressed overlayers. The films were spin coated onto a aluminized substrates to four thicknesses ranging from 24 nm to 11.8 μm. The indentation tests showed that the near surface properties of all four films were essentially the same. In contrast, susceptibility to fracture appeared to vary with film thickness where the thickest film delaminated readily during indentation while the thinner films required deposition of highly stressed overlayers to trigger delamination. Nevertheless, fracture in all samples occurred along the film substrate interface. Mechanics-based models were then used to determine interfacial fracture energies. In this presentation, the test and analysis techniques will be discussed and used to show that practical works of adhesion can be obtained for the very thin polymer films used in this study. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

4:00 PM Q6.4
EPOXY/ALUMINUM ADHESION AS MEASURED BY CONTACT MECHANICS (JKR) IN THE PRESENCE OF AN ORGANIC CONTAMINANT. John A. Emerson, Dara L. Woerdeman[a], Rachel K. Giunta, Sandia National Laboratories, Albuquerque, NM; [a]Virginia Commonwealth University, Richmond, VA.

Bonding of microassemblies gives rise to a variety of technical barriers, including dispensing, alignment, and fixturing. In these minute length scales, knowledge of interfacial properties such as roughness and surface energies of the various components is critical. Surface contamination is a common occurrence, and therefore calls for a convenient method to assess the cleanliness of the adherends before introducing adhesive to the microsystem. Photoelectron surface analytical techniques are routinely used for characterizing substrates, however they are impractical because the contaminants are vaporized in high vacuum. The JKR contact mechanics technique has a number of unique advantages for probing micron-scale areas in a processing environment, since it is relatively inexpensive, versatile, and easy to operate. In a theoretical study by Brochard-Wyart and de Gennes, they consider the dewetting phenomena of water between a hydrophobic solid and a rubber. In the present work, we investigate the behavior of a model organic contaminant, hexadecane, in contact with aluminum using AFM. We use hexadecane because it replicates typical machining fluids, is nonreactive with aluminum surfaces, and should not dissolve readily into the adhesive systems of interest. Preliminary results have shown that the hexadecane does not wet the aluminum oxide surface, but instead, forms a discontinuous film. Of particular interest is understanding why we observe dewetting of a low surface tension fluid in contact with a relatively high energy surface. We also examine the effect of the contaminant on the adhesive forces between an epoxy elastomer (the probe) and aluminized glass using the JKR contact mechanics approach. The extent of hysteresis in the contact mechanics curves illustrates the sensitivity of the technique to minute quantities of hexadecane on the surface. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

4:15 PM Q6.5

ADHESION OF A CYLINDER OR SPHERE TO AN INCOMPRESSIBLE FILM. Fuqian Yang[a,b] and J.C.M. Li[b]. [a]Xerox Corporation, Webster, NY. [b]Department of Mechanical Engineering, University of Rochester, Rochester, NY.

With the development of the surface force apparatus (SFA) such as the atomic force microscope, the use of SFA in conjunction with the JKR [1] and DMT [2] theories to study the adhesion of micro/nano-particles to a thin film has greatly improved our understanding of the molecular mechanisms involved. However, it is also open to potential error for the interfacial energy since both theories are based on the contact between two elastic spheres or the contact of a sphere and a half space. The present work extends these theories to the contact of a particle to a thin film deposited on a rigid substrate. The adhesion between a rigid flat cylindrical particle of radius a or a rigid spherical particle of radius a and an incompressible elastic film of thickness h has been studied. The contact surfaces between the particle and the film and between the film and the substrate are either frictionless (slip) or perfectly bonded (stick). Using integral equations, the stress distribution in the contact area was solved, which was used to obtain the load required to press the particle onto the thin film. The solutions for these cases give the upper and lower bounds for the real case in which the contact surfaces between the particle and the thin film and between the thin film and the substrate are neither frictionless nor perfectly bonded. Using the equilibrium thermodynamic method, developed by Johnson [1] and Derjaguin [2], the pull-off force to separate a rigid particle from an incompressible elastic layer are obtained numerically and analytically. For a rigid flat cylindrical particle and $a\ gg\ h$, the pull-off force is proportional to $a^{2}\ h^{-1/2}$ if it is frictionless on both contact interfaces. But the pull-off force is proportional to $a^{3}\ h^{-3/2}$ if it is frictionless between the particle and thin film and bonded between the thin film and the substrate. [1] K.L. Johnson, K. Kendall, and A.D. Roberts, Proc. R. Soc. London, A324(1971) 301 [2] B.V. Derjaguin, V.M. Muller, and Y.P. Toporov, J. Colloid Interface Sci. 53(1975) 314

4:30 PM *Q6.6

ADHESION OF INELASTIC SPHERICAL SOLIDS. K.L. Johnson, University of Cambridge, Cambridge, UNITED KINGDOM.

Spherically tipped micro and nano indenters are increasingly used to extract the surface energy and mechanical properties of solid surfaces, for which a mechanics model of the indentation and adhesive process is required. For elastic, reversible solids such models are well developed (e.g. JKR and DMT) but, for inelastic solids, the situation is more complex on account of the energy dissipated in the solid by viscoelastic or plastic deformation. In the viscoelastic case, it is well known that adhesion is rate dependent and that more external work is required to separate two surfaces than is extracted when they come together: so called "adhesion hysteresis". When plastic deformation takes place during indentation, adhesion on separation is modified and can take two forms: either "brittle" separation at the interface or "ductile" separation by the formation of a drawn out neck. The lecture will review progress in modelling these processes.

SESSION Q7: POSTER SESSION NANOINDENTATION AND NANOTRIBOLOGY

Chairs: Shefford P. Baker and Sean G. Corcoran
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

Q7.1

THE EFFECTS OF CREEP ON ELASTIC MODULUS MEASUREMENT USING NANOINDENTATION. Gang Feng, Alfonso H.W. Ngan, The University of Hong Kong, Department of Mechanical Engineering, Hong Kong, PR CHINA.

In nanoindentation the moduli of materials are usually calculated using the Oliver-Pharr scheme in which it is assumed that the unloading process is purely elastic. However, time dependent deformation (TDD) can happen alongside elastic recovery, and consequently, the modulus calculated may be over or underestimated. One form of TDD is thermal drift and this can be corrected for by subtracting from the observed displacement rate a thermal drift rate, which is measured in a low load hold period. Another form of TDD is creep. In this paper we show that creep always result in over-estimation of the modulus. We also present evidences showing that the effects of creep cannot be eliminated simply by using very long holding time, since even though steady state creep may be achieved, the creep rate is still larger than zero (e.g. about 0.05nm/s for Cu (111) plane under 6 mN). A method is proposed to correct for the effect of TDD by extrapolating the TDD law in the holding process to the unloading one if the TDD is assumed to exhibit either time-hardening or strain-hardening constitutive characteristics. Thermal drift is correctable by this method as it trivially obeys time-hardening conditions. Under this assumption, the error introduced by TDD in the contact compliance is shown to be equal to the displacement rate (creep plus thermal drift) at the end of the holding period divided by the unloading rate during the unloading process that follows. Thus very serious errors may be introduced if a short holding period or a slow unloading rate is used. This correction method is applied to compute the elastic moduli of three materials including single crystal copper, single crystal Ni_3Al and polycrystalline Al, and the results are compared with the values obtained without considering the TDD effects.

Q7.2

NANOINDENTATION AND NANOSCRATCHING OF SILICON CARBIDE ALLOYED PYROLYTIC CARBON. Martin A. Wiedenmeier, Sulzer Carbomedics Inc., Austin, TX; Steven G. Thomas, George M. Pharr, Univ of Tennessee, Dept of Materials Science and Engineering, Knoxville, TN and Oak Ridge National Laboratory, Oak Ridge, TN.

Pyrolytic carbon (PyC) alloyed with silicon carbide is the principle material used in the manufacture of mechanical heart valves. PyC is made by cracking hydrocarbon and silane gases in a fluidized bed reactor at relatively low temperatures (~1350C). The mechanical behaviour of films of PyC alloyed with up to 14 wt% silicon deposited on graphite substrates was examined by nanoindentation and nanoscratching with a Berkovich indenter. Several unusual behaviours were observed, including fully elastic contact at all loads (up to 300mN) and a sharp reduction in scratch resistance at silicon concentrations above ~8 wt%. Results are presented and discussed in terms of pertinent microstructural observations.
Research sponsored in part by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

Q7.3

NANO-INDENTATION OF THIN FILMS: EXPERIMENTS AND ANALYSIS. Kaiyang Zeng, Lu Shen, Institute of Materials Research and Engineering, SINGAPORE.

This work is focused on the nano-indentation of thin film materials. Several different thickness of Al_2O_3 film on Al, Al film on sapphire and Al film on Si were tested by nano-indentation techniques. The experiments covered two kinds of thin film structures: i.e., hard film on soft substrate, and soft film on hard substrate. It is generally believed that, for nano-indentation of thin films, the indentation depth should be less than 1/10 of the film thickness in order to avoid the effects of substrate to the measurement. This was examined through the current experiments. Our experiments showed that the maximum indentation depth, whereas no influence the substrate to the measurement, is in fact different from the cases of hard film on soft substrate to the soft film on hard substrate. This maximum depth is also controlled by the degree of differences between the film and substrate. The larger differences, the smaller the indentation depth. The results were also analyzed using the newly developed analysis method.

Q7.4
SURFACE FORCE DRIVEN CONTACT GROWTH BETWEEN VISCO-ELASTIC PARTICLES. A. Jagota, Dupont Co, Wilmington, DE; Y.Y. Lin, C.Y. Hui, Cornell Univ, Ithaca, NY.

The mechanics of surface force driven contact growth between viscoelastic particles show the presence of three distinct stages. The first is the formation of a contact governed by the marginal balance of stored elastic and surface energies. The third stage is one of sintering driven by surface tension. Contact growth in sufficiently small particles is predicted to be dominated by an intermediate 'zipping' mode driven by direct attraction across the gap ahead of the contact edge. The zipping mode of contact growth has been analyzed using results from the cohesive-zone theory of viscoelastic fracture and computationally using surface finite elements. Unlike the first and third stages of contact growth, the zipping stage depends on the details of the cohesive force distribution, specifically the characteristic cohesive stress. It is predicted to dominate contact growth kinetics for sub-micron particles. We will present exact and numerical results from this study, compared with existing theories and experimental data on the coalescence of polymeric particles.

Q7.5
MOLECULAR DYNAMICS SIMULATION OF ASPERITY SHEAR IN ALUMINUM. Jun Zhong, James B. Adams, Arizona State University, Dept. of Chemical and Materials Engineering, Tempe, AZ; Hualiang Yu, Arizona State University, Science and Engineering of Materials Program, Tempe, AZ.

One important mechanism of wear involves the shear of asperities by other asperities. Here we use molecular dynamics to simulate the shearing of aluminum asperities by a "hard" (Lennard-Jones) asperity. The simulations were repeated for a wide range of conditions, including different asperity drift velocities, temperatures, asperity shapes, degree of intersection, crystal orientations, and adhesive strength, to determine their effects on the wear process. These simulations involve the use of a reliable EAM potential for Al that was developed by Force Matching to a large database of DFT forces.

Q7.6
NANOINDENTATION EVALUATION OF BRITTLE FILMS ON HARD AND SOFT SUBSTRATES. Natalia Tymiak, Dept. of Chem. Eng. and Mat. Sci., University of Minnesota, Minneapolis, MN; Antanas Daugela, Hysitron Inc., Minneapolis, MN; Trevor F. Page, Materials Division, The University of Newcastle, Newcastle Upon Tyne, UNITED KINGDOM; William W. Gerberich, Dept. of Chem. Eng. and Mat. Sci., University of Minnesota, Minneapolis, MN.

In most cases, depth sensing indentation is the only practical means of evaluating the mechanical properties of thin films and coatings. While a number of experimental strategies and models for analysing data exist for general situations of this type, indentations into brittle porous films raise some added problems, not least because deformation of such films involves a variety of concurrent processes such as plasticity, densification, and fracture. As this poses quite a challenge for the experimental data interpretation, supplementary techniques such as acoustic emission become increasingly critical and useful. The present study addresses several cases of brittle films on different types of substrates. First, mechanical behavior of nanocrystalline SiC films on Mo substrates is considered. For the evaluation of indentation induced densification and intrinsic mechanical property deconvolution, repeated loading-unloading cycles have been utilized. This analysis was based on the P-d2 approach. With this method, indentation curves for elaso-plastic materials obtained with sharp pyramidal indenters may be represented as P=Kd2 where P, and d denote indentation load and displacement respectively. The parameter K includes materials hardness/modulus ratio and indenter geometry. This approach as applied to both loading and unloading enabled evaluation of mechanical property gradients through the film thickness. The method also allowed detection of transient events corresponding to indentation induced fracture. In addition acoustic emission (AE) was attempted to provide separation of deformation and fracture induced events. Second, yield initiation phenomena have been evaluated for oxidized W single crystal surfaces under normal and sliding contact with the assistance of AE as a supplementary technique.

Q7.7
3D FIB MAPPING OF CRACK ZONES IN Al_2O_3-SiC NANOCOMPOSITES. Timothy Steer, Houzheng Wu, Steve Roberts, Beverley Inkson, Dept of Materials, University of Oxford, Oxford, UNITED KINGDOM.

Al_2O_3 - SiC nanocomposites exhibit dramatically improved strength and wear properties compared to monolithic Al_2O_3 ceramics with similar grain sizes. In particular, in abrasive wear a transition from intergranular cracking in Al_2O_3 to intragranular cracking in Al_2O_3 - SiC nanocomposites is observed. This change in fracture mode results in a reduction in wear rate for the nanocomposites (no grain pullout) and improved surface finish. In order to investigate the mechanisms causing the change in fracture mode and near-surface damage behaviour during wear, Al_2O_3 - 5vol.% SiC nanocomposites and monolithic Al_2O_3 have been locally deformed by indentation. The subsurface damage beneath the indent sites has been analysed in 3D using a new 3D focused ion beam (FIB) mapping technique. This technique enables 3D maps of the cracks zones to be extracted, directly under the indents where the mechanical properties have been measured. Using this method, the 3D nature of the crack zones in the Al_2O_3 - SiC nanocomposites and monolithic Al_2O_3 may be directly compared.

Q7.8
STRESSES AND IMPACT TESTS FATIGUE OF PVD HARD COATINGS ON CEMENTED CARBIDES DEPENDEND ON COATING PARAMETERS. E. Lugscheider, O. Knotek, K. Bobzin, Materials Science Institute, University of Technology Aachen, GERMANY; T. Leyendecker, G. Erkens, CemeCon GmbH, Aachen, GERMANY; A. Bouzakis, Laboratory for Machinetools and Manufacturing Engineering, University of Thessaloniki, GREECE.

For quality control of PVD hard coatings applied on carbide machining or forming tools the scratch test gives a first impression of the adhesion under constant or increasing loads. Coated carbide machining tools are often working under dynamic load, which has a great influence on the adhesion properties of the hard coatings (TiAlN and C-based films). To get detailed information about the coatings characteristics and its dynamic behaviour the impact tester was developed and further improved. This test method is used for research and assement of failure mechanisms of thin films and statements about the adherence of hard material coatings under dynamic compressive stress. Therefore a hard metal ball strikes with a frequency of up to 50 Hz onto the surface. The altitude stress can be varied to get a detailed evaluation of fatigue under reversal strain. The appearance of surface fatigue is based upon structural transformation, cracking and cracking-growth processes and ends with the separation of debris particles caused by the above mentioned permanent changing strain. Selected hard material coatings were analyzed after testing with the described method. The results of the impact tests were compared with the measured data of the stress distribution by nanoindentation. It will be shown, that the results of the fatigue test and the adhesion properties are dependent on deposition parameters. Different types of hard coatings were analyzed and compared.

Q7.9
SPHERICAL INDENTATION AND FLOW PROPERTY MEASUREMENT-FINITE ELEMENT SIMULATIONS. Ming Y. He, G.R. Odette, Materials Department, University of California, Santa Barbara, CA.

Recently an automated ball indentation testing technique (ABI) to measure flow properties of metallic materials have been developed. It has been further developed to estimate yield strength and fracture toughness. In this method, the stresses and associated plastic strain are determined by the measured values of applied indentation load and associated residual indentation depth. To verify this testing technique computer simulations of the ball indentation by finite element analysis (FEA) have been performed. A range of prototypic true stress-true strain curves, including those reflecting the effects of irradiation, were used as input data for the simulations. The indenter was loaded and unloaded for many cycles, and the applied loads and associated displacements were obtained from FEA. The stresses and associated plastic strain determined using the ABI method were compared to the input constitutive equations. These comparisons show that for materials with moderate strain hardening (exponent N=0.1 to 0.3), the ABI estimates are in generally good agreement with the input stress-strain curves. However for lower strain hardening the ABI test did not accurately predict the strength. The upper and lower strain range limits of the ABI method was also determined.

Q7.10
NANOINDENTATION OF POLY (METHYL METHACRYLATE). Michael J. Adams, David M. Gorman, Simon A. Johnson, Unilever Research Port Sunlight, Bebington, UNITED KINGDOM.

It can be shown analytically that the load increases with the square of the total penetration depth for the indentation of both purely elastic and rigid-plastic homogeneous half-spaces with conical and pyramidal indenters. Loubet et al. [1] have shown that this relationship is also valid for an elastic-perfectly plastic half-space - they derived an expression for the loading curve in terms of material and geometric parameters and demonstrated its applicability to steel. Hainsworth et al. [2] extended this approach to other metals and sapphire and indicated how deviations from the quadratic behaviour could be used to investigate materials with depth or scale-dependent mechanical properties. Malzbender et al. [3] have very recently shown that the same result follows by simple manipulation of the standard equations currently used to analyse nanoindentation data. Results from finite element calculations showed excellent agreement with the analytical expression for the case of a material with relatively large values of the elastic modulus and hardness. In the current paper, it is shown how this approach can be extended to polymers. Experimental data are presented for the indentation of PMMA sheet with a Berkovich indenter. Each indentation was done using an exponentially-increasing loading rate in order to ensure that the imposed strain rate was constant as function of penetration depth [4]. A simple manipulation of the standard equations also allows the ratio of the contact depth to the total penetration value to be expressed in terms of material and geometric parameters. It is shown how this ratio can be used to aid the interpretation of creep and creep recovery data for viscoelastic materials. [1]. J.L. Loubet, J.M. Georges and G. Meille, in Microindentation Techniques in Materials Science and Engineering, eds. P.J. Blau and B.R. Lawn, ASTM, Philadelphia, p72 (1984). [2]. S.V. Hainsworth, H.W. Chandler and T.F. Page, J. Mater. Res. 11, 1987 (1996). [3]. J. Malzbender, G. de With and J. den Toonder, J. Mater. Res. 15, 1209 (2000). [4]. G. Hochstetter, A. Jimenez and J.L. Loubet, J. Macromol. Sci.-Phys. B38, 681 (1999).

Q7.11

CORRELATION OF NANOINDENTATION AND CONVENTIONAL MECHANICAL PROPERTY MEASUREMENTS. Philip M. Rice, IBM Research Division, Almaden Research Center, San Jose, CA; and Roger E. Stoller, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN.

A series of model ferritic and commercial alloys was used in an investigation of solute effects on radiation-induced hardening. The model alloys were irradiated with both light and heavy ions and subjected to various heat treatments to obtain a broad range of measured hardness values. Measurements on commercial alloys were used to further extend this range. Nanohardness measurements with loads as low as 0.05 g were obtained with the NanoIndenter-II and compared with conventional Vickers microhardness measurements using a 200 g load. Two methods were used to obtain the nanohardness data for the comparison with Vickers hardness: (1) constant displacement depth and (2) constant load. When the nanohardness data was corrected to account for the difference between projected and actual indenter contact area, good correlation between the Vickers and nanohardness measurements was obtained for hardness values between 0.7 and 3 GPa. The correlation based on constant nanoindentation load was slightly better than that based on constant nanoindentation displacement. Tensile property measurements were also made on these same alloys, and the expected linear relationship between hardness and yield strength was found. Thus, a correlation was developed between measured changes in nanohardness and yield strength changes.

Q7.12

MECHANISM OF AlCuFe QUASICRYSTAL PLASTIC DEFORMATION STUDIED BY INSTRUMENTED SHARP INDENTATION. Sergey N. Dub, Institute for Superhard Materials, Kiev, UKRAINE; Yuly V. Milman, Dina V. Lotsko, Anton N. Belous, Institute for Problems of Material Science, Kiev, UKRAINE.

Nanohardness tests of $Al_{65}Cu_{23}Fe_{12}$ quasicrystal reveals a different mechanism of plastic deformation as compared with a regular metal. For a metal, the indent depth increases monotonically with load, while for a quasicrystal, it increases stepwise. Penetration of the indenter into the metal occurs at the approximately constant average contact pressure. For quasicrystal the pressure under the Berkovich indenter is not constant. It growth during several seconds and that drop suddenly on about 300 MPa at 0.3 s. We think that the steps formation is not related to the indentation-induced cracks. Regular steps formation not observed for such brittle materials as sapphire, boron carbide and cubic boron nitride during loading up to 120 mN. Something close to these steps was observed earlier for germanium for which pressure-induced phase transformation in the indent takes place. Probably, the step formation in the load-displacement curve in AlCuFe quasicrystal is due to the structure transformation in the indent. It is known that the quasicrystal structure destroys at high deformation and transforms into a regular crystalline structure. Therefore, it is possible to attribute the pressure drop in the indent to the transformation of the quasicrystalline structure into the crystalline one. In this case the plastic polycrystalline metallic phase is pressed between a diamond indenter and a rather hard quasicrystalline bulk. In result, the plastic phase is extruded out of the indent and the pressure decreases. Then the pressure in the indent grows with the further loading until a new portion of the quasicrystal structure transforms into the crystal one. The observation of thin layers extruded out of the indent in AlCuFe quasicrystal supports this assumption.

Q7.13

DETERMINING THE INTERPHASE SIZE AND PROPERTIES IN POLYMER-MATRIX COMPOSITES USING PHASE IMAGING ATOMIC FORCE MICROSCOPY AND NANOINDENTATION. Lidvin Kjerengtroen, Dept of Mechanical Engineering, William Cross, Travis Downing, Rajneesh Kumar, and Jon Kellar, Dept of Materials and Metallurgical Engineering, South Dakota School of Mines and Technology, Rapid City, SD.

In polymer matrix composites the interface between the reinforcing phase and the bulk phase is paramount to the overall performance of the composite as a structural material. This interface is now thought to be a distinct, three-dimensional phase surrounding the reinforcing phase called the interphase. The development of the atomic force microscope and nanoindentation devices have facilitated the investigation of the interphase. Previously, force modulation AFM and nanoindentation were the primary methods used to determine the size of the interphase and its stiffness relative to the bulk phase. The present investigation utilized phase imaging AFM and nanoindentation to examine the interphase in a glass fiber-reinforced epoxy matrix composite. Nanoindentation experiments indicated that the relatively stiff fiber might have caused a gradient in the modulus across the interphase region. Specifically, the modulus next to the fiber approached that of the fiber and decreased to that of the bulk polymer as the distance away from the fiber increased. Once the fiber was removed by chemical etching this gradient reversed itself; hence, nanoindentation, due to the fiber bias, was not found to be adequate for measuring actual interphase properties. It was found that phase imaging AFM was a highly useful tool for probing the interphase, because it involves much lower interaction forces between the probe and the sample than force modulation or nanoindentation. The interphase in the model composite investigated was found to be softer than the bulk phase with a size of 2.4-2.9 microns, and was independent of fiber silane pretreatment, for silane pretreatments between 0.1% and 5.0% (initial aqueous concentration).

Q7.14

PLASTIC ZONE DEVELOPMENT AROUND NANO-INDENTATIONS. C.L. Woodcock, D.F. Bahr, Mechanical and Materials Engineering, Washington State University, Pullman, WA; N.R. Moody, Sandia National Laboratories, Livermore, CA.

Johnson's cavity model relating indenter geometry and deformation resulting from elastic-plastic indentations is appropriate for a wide variety of materials. In the case of nanoindentations in single crystal BCC metals, limitations are reached when creep is not fully accounted for. Both the standard Berkovich and cube corner geometries show changes in the ratio of plastic zone radius to contact radius increases with the duration of time at the peak load. Indenter tip geometry is shown to play an important role in this phenomenon. Length scale phenomena, such as the indentation size effect, are also subject to various interpretations. The traditional definition of hardness does not produce similar trends with indentation length scale between the blunt Berkovich geometry and the sharper cube corner tip. However, the ratio of the plastic zone radius to contact radius proves to be a tip geometry independent method of assessing the plasticity of these metals. These data are shown to hold for both low dislocation density materials (which exhibit a "yield point") as well as materials with large numbers of available dislocation sources in the region of the indenter tip.

Q7.15

NANOINDENTATION USING TUNNELING PROBE WITH SEMICONDUCTING DIAMOND TIP. Novikov Nikolai, Lysenko Oleg, Grushko Vladimir, Institute for Superhard Materials, Kiev, UKRAINE.

The mechanical properties of thin films can be measured by a variety of different techniques of depth sensing nanoindentation. At the nanometer level, the actual contact area must be carefully determined to obtain reliable values of mechanical properties by indentation. At this scale, the contact area is greatly affected by local surface roughness. Therefore an indendentation technique at the nanometer depth has to be associated with imaging technique. Measuring the topography of an indent using SPM and combining this information with a load-displacement nanoindentation data is one of the most recent developments in this growing field. Scanning tunneling microscopes or atomic force microscopes are used for imaging of surfaces before and after indentation. Simultaneously these microscopes with diamond tip have been used for indentation (atomic force microscopes are preferred because of their versatility). The disadvantage of the tunneling current measurement method is its limitation in studying materials with low conductivity. Increasing the tunneling probe sensitivity to the tunneling current up to the 0.01 nA can solve this problem. However in the case of traditional using a diamond tip for both indentation and scanning the obstacle of the low conductivity of a diamond arises. For a solution of this problem semiconducting diamond monocrystals were synthesized. A unique feature of this instrument is the ability to indentation at loads ranging from 0.00001 mN to 10 mN. The experimental procedure includes three main stages. At the first stage scanning the surface with an indenter makes a preliminary topographic image. At the second stage the indentation test is performed without the sample displacement. At the third stage the indented area is scanned again with the diamond tip in order to visualize the indent. The same tip is used for and sliding with further scanning of the surface. The relation between a-C:H films deposition parameters, the properties, and the surface morphology was studied.

Q7.16

MECHANICAL PROPERTIES OF ta-C FILMS PREPARED BY PULSED FILTERED VACUUM ARC DEPOSITION. W.F. Lau, S.P. Wong, N. Ke, W.Y. Cheung, Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, CHINA; X.Y. Wu, Institute of Low Energy Nuclear Physics, Beijing Normal University, Beijing, CHINA.

Hydrogen-free tetrahedral amorphous carbon (ta-C) films were prepared using a pulsed filtered vacuum arc deposition system at various substrate bias voltages. Thermal annealing was performed in vacuum at various temperatures. The sp3 fraction of the films was characterised by Raman spectroscopy. The Raman results confirmed that these ta-C films exhibited high sp3 fraction of over 80%. The hardness of the films was measured by the nano-indentation method. The friction and wear properties of the films were studied using a pin-on-disk tribometer. The stress in the films was studied by the curvature method while the stress distribution in the Si substrates was studied by the infrared photoelasticity method. The optical properties of the ta-C films were also studied using spectroscopic ellipsometry (SE). The complex refractive indices and the optical band gap of the ta-C films were obtained by analysing the SE spectra using the Forouhi and Bloomer model. Results on the issues such as the variations of the properties of these films with the deposition conditions and the film thickness, the stress relaxation with annealing conditions and the correlation between the mechanical properties and the sp3 fraction, will be presented and discussed. This work is partially supported by the Research Grants Council of Hong Kong SAR (Ref. No.: CUHK 4155/97E).

Q7.17

DETERMINING THE AREA FUNCTION OF SPHERICAL INDENTERS FOR NANOINDENTATION. Andrew J. Bushby[1], Nigel M. Jennett[2], [1]Department of Materials, Queen Mary and Westfield College, University of London, UNITED KINGDOM; [2]National Physical Laboratory, Materials Centre, Teddington, Middlesex, UNITED KINGDOM.

Nanoindentation with spherical tipped indenters provides a powerful technique for exploring surface 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. However, to be fully quantifiable and reproducible the technique requires accurate calibration of the indenter tip geometry. In nanoindention diamond indenters tend to be chosen for their high hardness and elastic modulus. However, the nominally spherical diamond indenters often deviate from an ideal spherical shape, due to the difficulty of polishing an anisotropic crystal into a perfectly spherical geometry. Significant errors may be introduced by using a constant (especially the nominal) radius in calculations. Use of a continuous function describing radius (or area) as a function of depth is usually necessary. Calculation of the effective shape, or area function, for pointed indenters is often based, for convenience, on indentation into reference materials. Methods using two reference materials have shown good agreement with direct imaging using atomic force microscope (AFM) techniques. In this paper indentation methods are used to characterise a range of spherical tipped indenters with nominal radii from 2 to 30 microns. A traceably calibrated metrological AFM is also used to determine the actual shape of one of the indenters. Comparisons of the two methods are made and the sensitivity of both methods to measurement parameters are discussed.

Q7.18

APPLICABILITY OF SNEDDON'S EQUATION TO THE ANALYSIS OF NANOINDENTATION DATA. I. Matthew, M. Tomozawa, Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY.

Sneddon derived equations that describe the elastic response of a flat specimen under a conical indenter. The Oliver and Pharr method of analysis of nanoindentation data applies these equations to the unloading data and evaluates the projected area of contact to determine the indentation hardness. Hardness values obtained by this method are observed to be independent of the maximum load. However, hardness values obtained by microhardness testing show an indentation size effect (ISE) where the hardness increases as the load decreases. Careful analysis of nanoindentation data obtained from different materials shows that Sneddon's equations do not apply over the entire range of indentation depths at which nano-indentation experiments were performed. Results show that the projected area of contact evaluated using this method (at maximum load) is larger than the cross-sectional area of the indenter for the same contact depth, even when the non-ideality of the indenter tip has been accounted for. This deviation in the projected area of contact at maximum load is a function of the indentation depth for a given material and is different for different materials. It has to be taken into account for accurate analysis of nanoindentation data.

Q7.19

NANOSCRATCH DEFORMATION RESPONSE OF CARBON NITRIDE THIN FILMS. C. Charitidis, P. Patsalas, S. Logothetitidis Aristotle Univ, Dept of Physics, Thessaloniki, GREECE.

Nanoscratch test provides a simple, versatile and rapid means of assessing the scratch resistance of thin films with thickness below 1μm, information on the surface elastic-plastic deformation modes and their adherence to the substrate. We investigate the scratch response of thin (200 nm) Carbon Nitride (CN_x) films, deposited on Si(001) by sputtering under intense ion irradiation, in the load range from 2 to 20 mN. The film mechanical performance was studied by nanoindentation and nanoscratching. We have found a load dependent transition in the scratch and friction responses. Below 5 mN, the scratches showed a completely elastic behavior. Above 10 mN the scratches showed a mixed elastic-plastic behavior and at 20 mN exhibited areas with permanent grooves. However, Atomic Force Microscopy and in-situ profiling of the surface of the film before, during and after the scratch event observed no evidence of film failure. Coefficient of friction (μ, between 0.1 and 0.3) and plastic deformation increased with increasing load (L). The relation between μ and L is given by an expression of the form $\mu = L^b$. The exponent b arises from the type (elastic, plastic) of film deformation after scratch test. The film recovery after nanoscratch testing at 10 mN manifested variations in slope, which correspond to different stages in the deformation of the CN_x film and hence determines transitions between different failure modes. The nanoscratching behavior of the CN_x films was correlated with their microstructure as it was studied by X-Ray Diffraction (XRD) and Reflectivity. XRD suggested that CN_x is not homogeneous, but there are crystalline grains embedded in an N-poor amorphous matrix. The latter is supported by Continuous Stiffness Measurements revealing considerable variations of hardness and elastic modulus values (local values up to 45 GPa and 230 GPa, respectively) indicating that the crystalline regions are superhard and elastic.

Q7.20

EFFECT OF FILM THICKNESS ON THE NANOINDENTATION MEASUREMENT OF SUPERHARD DIAMONDLIKE CARBON FILMS PREPARED BY PULSED LASER DEPOSITION. Q. Wei, J. Sankar, NSF Center for Advanced Materials and Smart Structures, Dept. Mech. Eng., NC A&T State Univ., Greensboro, NC; A.K. Sharma and J. Narayan, Dept. MS&E, NC State Univ., Raleigh, NC.

We have investigated the effect of the film thickness on the nanoindentation measurements of superhard diamondlike carbon films. The DLC films were deposited on Si (100) substrates by pulsed excimer laser (KrF, λ=248 nm, duration =25 ns, energy density about 3.0 J/cm^2) in high vacuum (exceeding 10^{-7} torr) at room temperature for various periods of time. The nanohardness and elastic modulus of these films were measured by Nanoindenter^{XP}. It was found that the nanoindentation results are a function of film thickness. In order to obtain more realistic mechanical properties of the DLC films, we used finite element analysis to model the nanoindentation process. Ansys5.5 was used to simulate the nanoindentation process to obtain the calculated load-displacement curves for the DLC films and the simulated results were fitted to be comparable to the experimental load-displacement curves. It was found that combination of nanoindentation experiments with finite element modeling can give more accurate information of superhard DLC films than nanoindentation tests alone.

Q7.21

NANOINDENTATION MEASURES OF POLYSTYRENE ADHESION. Min Li, C. Barry Carter, William W. Gerberich, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN; Marc A. Hillmyer, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN.

Indentation combined with atomic force microscopy (AFM) has been utilized for the evaluation of polystyrene (PS)/glass adhesion.

Adhesion energy calculations have been made using AFM measurements of the delaminations induced by indentation. To enhance the driving force for delamination, poly(methyl methacrylate) (PMMA) overlayers were applied on top of PS films. The PS (Mw=189K) film of thickness 0.66μ with a 1.5μ PMMA overlayer has a measured adhesion energy of $\sim$0.55J/m^2. Fracture surfaces were also characterized to provide insight into the mechanism of interfacial fracture. In addition, using a pull-off method, the effect of PS molecular weight on the adhesion energy between tip and PS was studied. Above a certain indentation load, low molecular weight PS appears to have a higher adhesion energy.

Q7.22
NANO-INDENTATION STUDIES OF LOW-K DIELECTRIC MATERIALS. Ashok Kumar, M. Anthony, I.M. Irfan, Center for Microelectronics Research, University of South Florida, Tampa, FL.

Low-K dielectric films have reduced hardness and modulus values relative to traditional dielectrics and they are many potential challenges associate with these materials to integrate with IC technologies. In this investigation, we have used nanoindentation studies to evaluate the mechanical properties of doped oxides dielectrics (FSG,HSQ, MSQ, HOSP), organic dielectrics (BCB, SiLK, FLARE, PAE-2), highly fluorinated dielectrics (paryleneAF4, a-CF, PTFE), porous dilectrics (aerogels, xerogels, nanogels.The structural properties of the films have been also investigated using analytical techniques.

Q7.23
THE EFFECT OF SURFACE FORCES ON APPARENT CONTACT COMPLIANCE AND THE IMPLICATIONS FOR FRAME COMPLIANCE DETERMINATION. Nigel M. Jennett[1], Andrew J. Bushby[2]. [1]National Physical Laboratory, Materials Centre, Teddington, Middlesex, UNITED KINGDOM. [2]Department of Materials, Queen Mary and Westfield College, University of London, UNITED KINGDOM.

Depth sensing indentation (DSI) is one of the few techniques capable of probing both the elastic and plastic responses of very small volumes, such as thin layers. For elasticity, DSI measures the total contact compliance, which is a composite of the mechanical responses of the instrument frame, indenter and all components of the sample. Isolation of the elastic response of the target material requires a precise and accurate determination of all other compliances in the contact. The determination of frame compliance, Cf, of DSI instruments is therefore a crucial pre-requisite for obtaining reproducible, quantified measurements of indentation modulus. Determination of Cf by indentation into a reference material is widely used and can be repeatable. It is shown, however that the Cf value produced is reference material dependent. Rearrangement of the contact mechanics equation has been suggested, but this introduces additional assumptions, such as hardness being invariant with depth. Often the same data gives different Cf values depending on the analysis used. In this paper we present results from the European Commission funded project: "Determination of hardness and modulus of thin films by nanoindentation - INDICOAT". Indentation experiments into a wide range of reference materials have been performed using Berkovich and large radius spherical indenters. Reliable direct measurement of indenter area functions and surface modulus values for reference materials are used, to allow more accurate subtraction of the contribution of the sample from the total contact compliance. However, the Cf values obtained in this way are load dependent and a may be described by a function of the area of contact. Supplementary experiments are described which show that surface forces affect the measured contact compliance. The implication of this for the determination of Cf are discussed.

Q7.24
NANOINDENTATION OF PRESSURE QUENCHED FULLERENES AND ZIRCONIUM METAL FROM A DIAMOND ANVIL CELL. Shane A. Catledge, Philemon T. Spencer, Jeremy R. Patterson, Yogesh K. Vohra, Dept. of Physics, University of Alabama at Birmingham, Birmingham, AL.

Due to the advent of diamond anvil cells, the physical properties of materials can be investigated under pressures of millions of atmospheres and temperatures of several thousand Kelvin. The sample size employed in these high pressure cells is limited to a diameter of typically 25 to 150 microns. While this size is often sufficient for diagnostics using synchrotron x-ray diffraction and Raman scattering, ex-situ measurement of mechanical properties using conventional microhardness indentation techniques is not feasible. For some materials, the high pressure phase(s) can be quenched to ambient pressure allowing further characterization by other techniques. In this paper, we make use of the very small probe volume allowed by nanoindentation to investigate the pressure-quenched structures of both C-70 fullerene and zirconium. For the case of C-70, we show that the amorphous phase established above 35 GPa can be quenched, and that it shows a largely elastic indentation loading behavior with a hardness of 18 GPa (compared to 7 GPa of the surrounding steel gasket). We establish that this hard carbon phase can be produced from C-70 fullerene by application of pressure at room temperature. Also of interest is the pressure quenching of zirconium metal from the unique omega-phase (hexagonal symmetry with AlB_2 structure). The use of pressure quenching in a diamond anvil cell along with subsequent nanoindentation of the small sample volume opens up new windows of opportunity for mechanical property measurements of materials after processing in high pressure-high temperature conditions.
Supported by National Science Foundation (NSF)

Q7.25
COMPUTER SIMULATION OF FRICTION OF POLYMER SURFACES. Dieter W. Heermann, Institut für Theoretische Physik, Universität Heidelberg, Heidelberg, GERMANY.

I propose a model to simulate friction of amporphous polymer surface. To model friction I use a tip-shaped tool that is dragged across the surface of a polymer film. In the contribution I focus on the region around the tip and exclude shear forces other than the internal. To be independent from the finite film thickness I introduce a coupling parameter κ which is measure of the frictional force. After that I examine the dependence of κ on the load, the angel of attack and the velocity of the tool. Finally I present the results of the structural modifications caused by the tool.

Q7.26
VIEWING A MOVING SURFACE CONTACT: A SCANNING PROBE MICROSCOPY AND QUARTZ CRYSTAL MICROBALANCE STUDY OF SLIDING FRICTION IN ADSORBED MOLECULES. B. Borovsky, T. Coffey, M. Abdelmaksoud, and J. Krim, North Carolina State University, Department of Physics, Raleigh, NC.

Experimental investigations of friction, lubrication, and adhesion at nanometer length scales have traditionally been performed by employing scanning probe microscopy (SPM), surface forces apparatus (SFA), or quartz crystal microbalance (QCM) techniques. The QCM has yielded quantitative information on fundamental energy dissipation mechanisms associated with the sliding friction of atoms along surfaces, but its results have never been cross-referenced with SPM or SFA measurements. In order to perform such a cross-referencing, we have carried out two investigations: (1) a STM-QCM study of tricresylphosphate (TCP) as well as a tertiary blend of phenol phosphates (TBPP), two common molecular additives with known lubricating properties on the macroscopic scale, and (2) a study, using several techniques, of the changes in interfacial friction of toluene on single crystal substrates in both the presence and absence of C60 adsorbed layers. In the first study, the results of previous macroscopic friction measurements [1] have been correlated with sliding friction measurements obtained by means of a joint STM-QCM apparatus.[2] In the second study, the results of previous SFA measurements [3] have been correlated with AFM, QCM and macroscopic contact angle [4] measurements.
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[2] Borovsky, B., Mason, B.L., and Krim, J., "Scanning Tunneling Microscope Measurements of the Amplitude of Vibration of a Quartz Crystal," submitted to *Journal of Applied Physics*.
[3] Barrat, J.L. and Bocquet, L. (1999), "Large Slip Effect at a Nonwetting Fluid-Solid Interface," *Physical Review Letters*, **82**, 4671-4674.
[4] Campbell, S.E., Luengo, G., Srdanov, V.I., Wudl, F., and Isrealachvili, J.L. (1996), "Very low viscosity at the solid-liquid interface induced by adsorbed C60 monolayers," *Nature*, **382**, 520-522.

SESSION Q8/W6: JOINT SESSION
LIMITS OF STRENGTH IN INDENTATION
Chairs: Murray S. Daw and Joost J. Vlassak
Thursday Morning, November 30, 2000
Room 309 (Hynes)

8:30 AM *Q8.1/W6.1
EXPERIMENTS ON THEORETICAL STRENGTH AND SIZE EFFECTS IN NANOINDENTATION. William D. Nix, Ranjana Saha, Erica T. Lilleodden, David Barbero and Bruce M. Clemens, Department of MS&E, Stanford University, Stanford, CA.

Nanoindentation permits the study of plasticity of materials in very small volumes, from the atomic and molecular scale, through the mesoscopic scale to the continuum scale. As such it provides a particularly good tool for validating the predictions of multiscale modeling and simulation of material behavior. Various plasticity experiments at small length scales will be described. Here we consider Individual Dislocation Effects, involving the nucleation of dislocations in perfect crystals and Multiple Dislocation Effects, as revealed by various indentation size effects. Nanoindentation of Mo and Ta epitaxial films and Au single crystals at the nanometer depth scale reveals irregular load-displacement curves that appear to be associated with the nucleation of dislocations. The contact pressures at which the first inelastic events are triggered compare favorably with recent calculations of nanometer scale indentations in perfect crystals. We show that these discrete plastic events are strongly affected by the proximity of high angle grain boundaries, suggesting that grain boundaries can play a role in dislocation nucleation. We have shown that the indentation size effect on hardness of crystalline materials can be accurately modeled using the concept of geometrically necessary dislocations and that this can be used to formulate a law for strain gradient plasticity. Here we describe a new type of nanoindentation experiment to show the effect strain gradients on flow strength. A strong plastic strain gradient is created by indenting a soft metal film on a hard substrate with a sharp diamond indenter. The hardness of the film is observed to increase with increasing depth of indentation, in sharp contrast to the falling hardness with increasing depth in bulk materials. We associate this rise in hardness with the strong gradient of plastic strain created between the indenter and the substrate and show that it can be calculated using a recently developed model of strain gradient plasticity.

9:00 AM Q8.2/W6.2

CONNECTING ATOMISTIC AND EXPERIMENTAL ESTIMATES OF IDEAL STRENGTH. C.R. Krenn[1,3], D. Roundy[2,3], Marvin L. Cohen[2,3], D.C. Chrzan[1,3] and J.W. Morris Jr.[1,3]. [1]Univ of California at Berkeley, Dept of Materials Science and Mineral Engineering. [2]Univ of California at Berkeley, Dept of Physics. [3]Lawrence Berkeley National Laboratory, Materials Sciences Division.

Using *ab initio* techniques, it is now possible to calculate the ideal shear strengths of perfect crystals with considerable accuracy. Using nanoindentation techniques, it is also possible to experimentally apply stresses of the order of the ideal shear strength to defect free regions of high purity single crystals. However, realistic determination of the stress fields produced during high stress nanoindentation requires finite element modeling. We use a finite element model incorporating a nonlinear stress-strain curve of the same form as that calculated *ab initio* for bcc tungsten to determine the maximum shear stresses reached beneath a stiff spherical indenter on a nonlinear elastic substrate. This model yields a load-displacement curve very similar to a Hertzian linear-elastic solution, but the peak shear stresses beneath the indentor are only 70% of those obtained from the Hertzian solution. We use these results to compare *ab initio* ideal strengths with the maximum shear stresses reached during nanoindentation of tungsten and molybdenum by Nix *et al.* and Gerberich *et al.* and find very good agreement. We conclude that the upper limit of strength during nanoindentation of initially defect-free tungsten and molybdenum is governed by the limits of elastic stability and suggest that other materials may behave similarly.

9:15 AM Q8.3/W6.3

THE ROLE OF MICROSTRUCTURAL LENGTH-SCALE IN INDENTATION BEHAVIOR OF GOLD. Erica T. Lilleodden, William D. Nix, Stanford University, Dept of MS&E, Stanford, CA.

Observations of depth dependent hardness have been made for various metals, and have been well described, in part, by strain gradient constitutive laws. However, strain-gradient models maintain a continuum framework and cannot be expected to explain discrete load-displacement behavior widely observed at the nanometer scale. Such observations of discontinuities in the initial stages of indentation imply that dislocation nucleation occurs, in agreement with atomistic calculations. However, the two descriptions, strain gradient analyses and dislocation nucleation considerations, rely on opposing limits of the relation between dislocation density and strength, imparting a critical discrepancy between these models. Here, we present experimental evidence of indentation size effects in hardness for gold thin films of various thicknesses. The observations are described in terms of dislocation nucleation and activation, and classical relations between dislocation distributions and strength. It is shown that the grain size affects both the critical loads for the onset of dislocation activity and the evolution of hardness with indentation depth. In particular, a Hall-Petch type strengthening mechanism is shown to play a substantial role in the indentation size effect of the small-grained films, overwhelming the strain gradient effects. Additionally, the competition between dislocation nucleation and activation of pre-existing dislocations is related to the grain structure and the proximity of the indentation to the grain boundary.

9:30 AM Q8.4/W6.4

PHYSICAL ORIGIN OF A SIZE EFFECT IN NANO-INDENTATION. A.J. Bushby[1], J.R. Downes[2], N.B. Jayaweera[2], P. Kidd[2], A. Kelly[3] and D.J. Dunstan[2]. [1]Department of Materials. [2]Department of Physics, Queen Mary and Westfield College, University of London, UNITED KINGDOM. [3]Department of Materials Science and Metallurgy, University of Cambridge, UNITED KINGDOM.

We have reported results of nanoindentation using spherical indenters to observe the full stress-strain curve. We observe the onset of plasticity in semiconductor strained-layer superlattices. These structures have alternating layers with strains of opposite sign. The yield pressure is reduced by the presence of the coherency strain. By varying the thicknesses and strains, we have been able to show that both sets of layers, compressive and tensile, reduce the yield pressure. This requires that a yield criterion must be satisfied over a finite volume, large enough to include layers of both sign. In these studies, we have observed a large and reproducible size effect in the yield pressure. That is, with smaller radius indenters the mean pressure acting over the contact area at the deviation from purely elastic behaviour increases, by up to a factor of two for a 2 micron radius indenter tip. Here we show how the requirement of meeting a yield criterion over a finite volume naturally leads to the size effect. Essentially, with small radius indenters, the peak stresses must be greater in order to achieve a given average stress over a finite volume. A theoretical analysis is given and quantitative agreement with experiment is obtained. This is a crucial result for the understanding of nanoindentation and other systems in which stresses are highly inhomogeneous on a small scale.

9:45 AM Q8.5/W6.5

IN-SITU NANOINDENTATION OF TRANSITION METAL CARBONITRIDES IN A TRANSMISSION ELECTRON MICROSCOPE. A.M. Minor, Department of MS&E, University of California, Berkeley, CA and Center for Advanced Materials, Lawrence Berkeley National Laboratory, Berkeley, CA; E.A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; C.R. Krenn, J.W. Morris, Jr., Department of MS&E, University of California, Berkeley, CA and Center for Advanced Materials, Lawrence Berkeley National Laboratory, Berkeley, CA.

The mechanisms of nanomechanical deformation in ultrahard materials such as the transition metal carbonitrides are poorly understood. We have recently developed a nanoindentation TEM specimen holder which gives us the ability to make real-time observations into the nanomechanical response of various materials. We will show results from real-time nanoindentations of transition metal carbonitrides and the subsequent analysis of the resulting indentation damage. Our results will be compared to prior *ex-situ* indentations of ultrahard materials, and to ongoing theoretical calculations of the ideal strength of these materials. We will also discuss issues related to the experimental procedures, including the unique specimen geometry required for the *in-situ* nanoindentations and the effects of the thin foil on the indentation.

10:30 AM Q8.6/W6.6

MECHANICAL RESPONSE OF DIAMOND AT NANOMETER SCALES: DIAMOND POLISHING AND AFM. Rubén Pérez, Murray R. Jarvis and Michael C. Payne, Universidad Autonoma de Madrid, Departamento de Fisica Teorica de la Materia Condensada, Madrid, SPAIN; University of Cambridge, Theory of Condensed Matter, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Many technological processes and characterization techniques rely on the mechanical response of materials at the nanometer scale. Although computationally demanding, ab-initio methods can now be used to explore the limits of strength under these conditions. In this work, total energy pseudopotential methods are used to study two different processes involving the mechanical interaction of diamond nanoasperities and diamond surfaces: the wear processes responsible for diamond polishing, and the mechanical deformation of tip and surface during the operation of the Atomic Force Microscope in contact mode (CM-AFM). The strong asymmetry in the rate of polishing between different directions on the diamond (110) surface is explained in terms of an atomistic mechanism for nano–groove formation. Although the direct ab-initio simulation of nanogrooving is still out of reach, the process can be studied in two steps. Separate simulations in which a rigid tip was incident from the soft and the hard polishing directions on a single nano–asperity show pronounced differences in the extent of the induced deformation. Then these differences in asperity removal are related to the process of nanogrooving by changing the boundary conditions at the edge of the asperity to recreate an ideal surface. The post–polishing surface morphology and the nature of the polishing residue predicted by this mechanism are consistent with experimental evidence. In the case of CM-AFM, it is shown that it is possible for a tip terminated in a single atom to sustain forces in excess of 30 nN. The magnitude of the normal force was unexpectedly found to be very similar for the approach on top of an atom or on a hollow position on the surface. This behaviour is due to tip relaxations induced by the interaction with the surface. These forces are also rather insensitive to the chemical nature of the tip apex.

10:45 AM Q8.7/W6.7

SINGLE CRYSTAL INDENTATION: OXIDE RUPTURE, SURFACE ASPERITIES AND THE YIELD POINT PROCESS. Donald E. Kramer, National Institute of Standards and Technology, Gaithersburg, MD; Karl B. Yoder and William W. Gerberich, University of Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN.

Nanoindentation of metallic single crystals has been a topic of recent investigations. This is a result of their ability to withstand near theoretical contact stresses without showing signs of plastic deformation. When plasticity occurs, it manifests itself as a yield point, a sudden discontinuous increase in indenter displacement and decrease in contact pressure. It has been suggested that dislocation nucleation is the controlling mechanism for the time dependent and instantaneous injection of plasticity under these conditions, while the importance of an oxide or contamination layer has been relatively unexplored. This study combines atomic force microscopy (AFM) with nanoindentation to demonstrate the roles that oxide films and asperities play in the yield point process. Time dependent and instantaneous yield point properties were investigated for single crystals of tungsten and Fe 3%-Si. AFM observations indicate that the presence of asperities has a dramatic effect on the time dependent yield point properties. Measurements on the dependence of yield point load on oxide film thickness are used to develop a fracture mechanics based model in which oxide film fracture controls the yield point process. The results suggest that dislocation nucleation can occur prior to a yield point, but that egress of these dislocations is inhibited by the oxide film. Upon fracture of the oxide film, this constraint is lifted and elastic/plastic indentation ensues.

11:00 AM Q8.8/W6.8

EFFECT OF SURFACE STEPS ON DISLOCATION STRUCTURE DURING NANOINDENTATION. Jonathan A. Zimmerman, Patrick A. Klein, Stephen M. Foiles, Sandia National Laboratories, Livermore, CA.

The study of dislocation nucleation and plastic behavior during nanoindentation is a prime example in which nanoscopic details play an important role in the evolution of macroscopic mechanical behavior. Experimental studies of nanoindentation suggest that the presence of surface irregularities, such as steps, modify the mechanical response during indentation. However, the experiments did not reveal the details of dislocation creation or how the nucleation process is altered by the irregularities. Through quasi-static atomistic simulations using the embedded atom method, we examine the indentation of a Au(111) crystal that contains a surface step. These simulations show the effect the presence of the step has on both global quantities of indentation force and mean pressure as well as the local atomic stresses. A newly formulated atomistic deformation metric, the slip vector, is used to quantify initial dislocation content. Using this metric, we analyze the shear stresses resolved onto the directions of the partial dislocations that form, improving upon previous analyses which have used the maximum resolved shear stress of all possible slip directions. Our analysis leads to an estimate of critical resolved shear stress to be used as part of a nucleation criterion even at very close distances to atomic-level defects, such as a surface step. In addition, the pre-nucleation stress fields are compared with continuum calculations performed using Cauchy-Born elasticity. These results show that the Cauchy-Born constitutive model works well even at the large deformations close to the indenter. The use of this model in conjunction with a coupled atomistic-continuum approach would allow simulation of systems much closer in size to those studied in experiments.

11:15 AM Q8.9/W6.9

IDENTIFICATION OF PRESSURE-INDUCED PHASE TRANSFORMATIONS USING NANOINDENTATION. Vladislav Domnich, Univ of Illinois - Chicago, Dept of Mechanical Engineering, Chicago, IL; Yury Gogotsi, Drexel Univ, Dept of Materials Engineering, Philadelphia, PA.

Depth-sensing indentation has been successfully used for identification of pressure-induced phase transformations in several brittle materials. Phase transformations during nanoindentation may be revealed through deviations in the shape of load-displacement curves from that of a perfect elastoplastic material. A sudden volume change during fast transformation results in the discontinuity in the load-displacement curve ("pop-in" or "pop-out" events). Sluggish transformation is followed by a gradual change in the slope of the loading or unloading curve (an elbow), which may not always be readily identified if the indentation data are presented as the load-displacement curves. Based on the empirical power law relation between the applied load and the elastic part of the indenter displacement, the average contact pressure (Meyer's hardness) during indentation can be assessed as a function of the contact depth between the indenter and the specimen. Defined in this manner, the pressure - depth relation is linear unless the elastic modulus of the specimen changes in the process of indentation. This greatly facilitates monitoring of possible phase transformations under the indenter and allows assessing the corresponding transformation pressures. Phase changes after indentation are verified by Raman microspectroscopy. The technique is applied to the studies of several single crystal semiconductors and ceramics, including silicon, germanium, boron carbide and zirconia.

11:30 AM Q8.10/W6.10

MECHANICAL DEFORMATION OF CRYSTALLINE SILICON DURING NANOINDENTATION. Jodie Bradby, J.S. Williams and J. Wong-Leung, Australian National University, Department of Electronic Materials Engineering, RSPhySE, Canberra, AUSTRALIA; M.V. Swain, University of Sydney, Biomaterials Science Research Unit, Department of Mechanical and Mechatronics Engineering and Faculty of Dentistry, Eveleigh, NSW, AUSTRALIA; P. Munroe, University of New South Wales, Electron Microscope Unit, Sydney, NSW, AUSTRALIA.

Deformation during spherical and pointed indentation in (100) crystalline silicon using a UMIS-200 nanoindenter has been studied using cross-sectional transmission electron microscopy (XTEM), atomic force microscopy and Raman microspectroscopy. XTEM samples were prepared by focussed ion beam milling to accurately position the cross-section through the indentations. Indentation loads were chosen below and above the yield point for silicon to investigate the modes of plastic deformation. Slip planes (originating from the region of maximum shear stress) are visible in XTEM micrographs for all indentation loads studied but slip is not the main avenue for plastic deformation. A thin layer of poly-crystalline material has been identified (indexed as a high pressure phase from diffraction patterns) on the low load indentation, just prior to yield ('pop-in' during loading). For loading above the yield point, a large region of amorphous silicon was observed directly under the indenter when fast unloading conditions were used. The various microstructures and phases observed below indentations are correlated with load/unload data.

11:45 AM Q8.11/W6.11

AN ASSESSMENT OF THE MICROSTRUCTURES AND MECHANICAL STRENGTHS OF ALUMINIDE-BASED THIN COATINGS. S.Y. Li, H.P. Ng and Alfonso H.W. Ngan, Univ of Hong Kong, Dept of Mechanical Engineering, Hong Kong, PR CHINA.

Titanium and nickel aluminide-based thin coatings were synthesized by magnetron sputtering from intermetallic Ti-50at.%Al and Ni-25at.%Al alloy targets on various substrate materials. Both of the aluminide coatings exhibited high surface hardness values that varied with the degree of heat treatment. Structural characterizations using atomic force microscopy and transmission electron microscopy revealed a typical nanocrystalline structure in the coatings. The hardnesses of the coatings were investigated over a wide range of applied loads using micro- and nano- indentation techniques. It was found that the measured hardness of the coatings depends on the indentation depth, the film thickness as well as the strength of the substrates. In order to estimate the intrinsic strength of the films, the indentation size effects of the apparent hardness were analyzed in terms of the "absolute hardness" models by Jonsson and Hogmark (1984) and Ngan and Ng (submitted). The Jonsson-Hogmark model is more applicable to the situation of hard, brittle films on soft substrates, while the Ngan-Ng model is applicable to soft films on either soft or hard substrates. The analysis indicated that the strengths of the aluminide coatings considerably exceed their strengths in bulk. Plausible strengthening mechanisms are discussed.

SESSION Q9: NANOTRIBOLOGY

Chairs: Trevor F. Page and Robert F. Cook
Thursday Afternoon, November 30, 2000
Room 309 (Hynes)

1:30 PM *Q9.1

FUNDAMENTAL ASPECTS OF FRICTION AND WEAR CONTACTS IN W,TA AND V SURFACES. W.W. Gerberich, N.I. Tymiak, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN; S. Downs, Hysitron Inc., Edina, MN.

Unexpected friction and wear transitions occur in transition metals associated with dislocation emission, dislocation storage, and oxide break-thru phenomena. Both normal nanoindentation and nanoscratch evaluations of conical diamond tips driven into tungsten, tantalum and vanadium {100} single crystal surfaces are being conducted. These represent the high, medium and low Peierl's barriers for dislocation motion in transition metals. Both quasi-equilibrium and kinetic aspects will be reported along with current but speculative ideas on multiple friction and wear transitions. Preliminary results show that yielding under contacts can be substantially different than normal contacts. For example, whereas a normal contact into {100}W might produce a 100 nm displacement excursion upon large scale dislocation release, a 100nm/s sliding contact at the same load can produce a 250 nm displacement excursion. Ramifications are seen in terms of friction coefficients which can double during the near-instantaneous yield excursion, but then continue to triple from about 0.05 to 0.15 in the pile-up phase in front of the sliding contact. Implications of how nanotribological issues such as adhesion connect thru this mesoscale activity to macroscopic friction and wear are discussed.

2:00 PM Q9.2
FEW ATOMS CONTACTS AND LIQUID LAYER FRICTION MEASURED BY AN ULTRA-HIGH SENSITIVITY AFM.
Peter M. Hoffmann, Steve Jeffery, Ralph A. Grimble and John B. Pethica, University of Oxford, Department of Materials, Oxford, UNITED KINGDOM; Ahmet Oral and H. Ozgur Ozer, Department of Physics, Bilkent University, Ankara, TURKEY.

An interferometry based ultra-high sensitivity AFM technique was used in both UHV and liquid to investigate sub-nanoscale mechanical properties. We present recent results from UHV experiments showing the mechanical behavior of a few atom contact between a metal tip and clean semiconductor or metal surfaces. It is seen that atomic rearrangements occur once the elastic energy stored in the contact exceeds a critical value of the order of about 1 eV/atom. Other useful parameters can also be extracted and the limits of simple analytical models to describe the obtained results are discussed. We have also carried out experiments in liquid, in which we measure the variation of lateral stiffness as a function of separation. We find that, in a liquid which is known to undergo ordering at solid surfaces, there are periodic variations in the lateral stiffness with separation corresponding to the molecular dimensions. In these experiments, we are able to examine the mechanical behaviour of a lubricating film on the molecular scale prior to the onset of frictional sliding.

2:15 PM Q9.3
INFLUENCE OF TIPRADIUS AND SUBSTRATE ON THE NANOTRIBOLOGICAL CHARACTERIZATION OF THIN DLC COATINGS. Th. Staedler, K. Schiffmann, Fraunhofer Institute for Thin Films and Surface Engineering, Braunschweig, GERMANY.

In this work DLC films with thicknesses of 20 and 250 nm on different substrates are characterized by nanoindentation and microscratching in combination with scanning probe microscopy. The substrates (SU8 photoresist, quartz glass, Si(100) and AlTiC ceramic) include very soft (hardness of SU8 photoresist = 0.4 GPa) up to very hard (hardness of AlTiC ceramic = 30 GPa) materials providing a wide range of combinations between film and substrate properties (typical hardness of DLC = 27 GPa). The experimental configuration allows the testing of samples with loads between 0.001 and 10 mN and a high local resolution. The tribological response of the various film/substrate systems is analysed in two different ways. On the one hand a single scratch test with linear increasing load is used and on the other hand the samples are exposed to oscillating wear tests at constant loads. The tip radii of the conical diamond tips utilizes in these experimental configurations vary between 0.5 and 8 micrometer. Both, the substrates as well as the tip radii, show a significant influence on the tribological behavior of the systems. Experimental results of the remaining wear depth, the friction coefficient, the critical load of an onset of irreversible surface deformation as well as the critical cycle number of complete film failure are correlated to parameters of the tribological system like substrate properties, tip radius and film thickness.

2:30 PM Q9.4
MECHANICAL AND MOLECULAR FILM PROPERTIES OF Si_3N_4 AND Y_2O_3-ZrO_2: A COMPARATIVE STUDY. Paul M. Jones, Seagate Research, San Jose, CA; James Kiely, Yiao-Tee Hsia, Seagate Research, Pittsburgh, PA.

Magnetic recording media are thin film overcoated to improve both their mechanical reliability and to create a chemically inert layer. Typical overcoats are comprised of sputtered carbon with various degrees of either Hydrogen or Nitrogen doping. Due to increasingly stringent recording requirements these protective layers are approaching one nanometer in deposited thickness. Both Si_3N_4 and Y_2O_3 stabilized ZrO_2 films present an alternative path to these typical overcoats. Si_3N_4 is in general use as a dielectric-encapsulant in magneto-optical media applications and Y_2O_3-ZrO_2 has previously been used as an overcoat on magnetic media (~200 - 300Å). Molcular calculations using all electron Density Functional Theory (DFT) were performed using cluster models of Si_3N_4, ZrO_2 and C(Diamond) crystalline forms. The derived electronic density of states provides indications of the degree of covalency in these idealized structures and also the degree of charge transfer. An effort is made to relate the results of the electronic structure calculations to properties, such as cohesive energy and hardness. Predictions of mechanical properties from DFT are compared with nanoindentation measurements of hardness and wear resistance. In an effort to approach theoretical properties, measurements were performed on single crystals of modeled materials, including Si_3N_4 and ZrO_2. These results were extended to microscopic wear testing of manufacturable materials (i.e., sputtered thin films on magnetic media) to give a better understanding of the relationship of DFT predictions and nanoindentation to material performance currently in use.

2:45 PM Q9.5
COMPUTATIONAL NANOTRIBOLOGY: SAMS FOR MEMS.
R.J. Berry, J.P. Moore, A.N. Davis, M. Schwartz, R.K. Bharadwaj, Materials & Manufacturing Directorate, AFRL/MLBP, Wright-Patterson AFB, OH.

Self assembled monolayers (SAMs) consisting of hydrocarbon and fluorocarbon chains attached to silica walls were evaluated computationally for their high temperature stability, life cycle and performance for MEMS aerospace applications. High level ab initio calculations of sufficient accuracy were conducted on model compounds to predict the bond strengths holding the monolayer tethered to the MEMS device and relate them to its thermal stability. Non-equilibrium molecular dynamics (NEMD) simulations under sliding periodic boundary conditions were employed to compute the frictional force as a function of applied load. The NEMD trajectories were analyzed for the structure and chain dynamics of the SAMs and compared with equilibrium MD results for the SAMs and fluid. The significance of monolayer penetration depth, monolayer gauche fraction, wall thermostat characteristics and the size of the simulation box on the computed results will be discussed.

3:30 PM *Q9.6
MOLECULAR TRIBOLOGY OF HIGHLY ORDERED MONOLAYERS. D. Gourdon, University of Santa Barbara, Santa Barbara CA; C. Duschl, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND; N.A. Burnham, Department of Physics, Worcester Polytechnic Institute, Worcester MA.

In order to investigate friction at a fundamental level, atomic force microscopy (AFM) in the wearless regime was performed on a model system - a highly ordered thiolipid monolayer on mica. In the monolayer, condensed domains with long-range orientational order were present. These domains revealed strong friction anisotropies as well as non-negligible asymmetries in the quasistatic friction loops. The directionality of these two effects appeared to correlate well with the tilt direction of the molecules (more specifically of their terminal alkyl chains) in the monolayer. The molecular tilt responsible for the strong frictional effects was surprisingly small - less than fifteen degrees - demonstrating that even small tilts can make a major contribution to friction at the molecular scale. The friction was measured on our model system as a function of applied load. The measurements versus load revealed two or three different frictional regimes (depending on the load range), that correlated well with a systematic stepwise behavior of the height of the domain as measured simultaneously. These discrete effects were attributed to molecular gauche defects created under the stress applied by the tip. Other studies include the friction as a function of sliding velocity, chemical preparation of the tip, alternative monolayers, and substrate. Our work suggests that friction on this system is primarily a mechanical phenomenon.

4:00 PM Q9.7
FRICTION MEASUREMENTS OF MOLECULARLY THIN LUBRICANT FILMS USING QUARTZ CRYSTAL RESONATORS.
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Although physics has dealt with the issue of friction since Amonton, its understanding still is mostly phenomenological. It was only recently that the classical friction laws have been put into perspective because of investigations with the Scanning Force Microscope and the Surface Forces Apparatus. Typical surface speeds of these methods are approximately 1 mm/s, and frequencies are in the range of f =

0.01-100 Hz.
For lubrication purposes polymers are often in use. Because of their fluid properties they reduce energy loss and wear of the surfaces that is caused by friction. In modern applications ultrathin (d < 30 Å) films are frequently required. However, due to this confined geometry many polymers lose their fluid properties (boundary-lubrication). Perfluoropolyethers are molecular lubricants that keep these properties even when subjected to extreme working conditions (speeds ≈ 1 m/s). We developed a quartz resonator method that comes very close to these conditions. Using quartz crystal resonators, the dependence on film thickness of the frictional properties of molecularly thin (d = 4-35 Å) perfluoropolyether films was investigated. For complete monolayer coverage (d > 25 Å) no energy loss in friction is detectable. It increases, however, with decreasing film thickness although the surface stays completely wetted.

4:15 PM Q9.8
STRUCTURAL CHARACTERIZATION OF THE NEAR-SURFACE PLASTIC DEFORMATION OF SEMICRYSTALLINE POLYMER BLENDS.
Houxiang Tang, David C. Martin, The Univ. of Michigan, Dept of Materials Science and Engineering, Ann Arbor, MI.

Near-surface deformation was introduced to polymer blends with a Teledyne Taber scratch testing apparatus. The deformation field was characterized by polarized light optical microscopy, microfocus pinhole X-ray difraction, scanning electron microscopy(SEM), and transmission electron microscopy (TEM). Images of the change in birefringence due to plastic deformation were obtained around the scratch, from which a mapping of the polymer chain orientation could be obtained. The localization of the deformation into shear band structures around the scratch was revealed through TEM imaging. Micromechanic model describing the nucleation and movement of the shear bands will be discussed. Geometrical parameters such as the scratch width, scratch depth, and recovered scratch depth were correlated with the anisotropy in the macroscopic mechanical properties of materials tested.

4:30 PM Q9.9
TRIBOLOGY OF ALKANE MONOLAYERS: THE EFFECTS OF TIP FLEXIBILITY AND DEFECTS.
Judith A. Harrison, Paul T. Mikulski, and Alan B. Tutein, United States Naval Academy, Chemistry Department, Annapolis, MD; Steven J. Stuart, Clemson University, Chemistry Department, Clemson, SC.

The molecular structure, mechanical properties, and tribological properties of self-assembled monolayer (SAM) materials have been studied a great deal using scanning probe microscopies due to their potential usefulness as boundary-layer lubricants. Salmeron and coworkers were among the first to suggest that the measured friction in these systems was linked to the energy dissipated by the formation of gauche defects. With that in mind, we have used molecular dynamics (MD) and a new, adaptive intermolecular reactive empirical bond-order potential (AIREBO) to examine friction in monolayers composed of n-alkane chains. Particular attention was paid to the formation of gauche defects and to the quantification of their contribution to the total energy dissipated during sliding. In addition, the utility of carbon nanotubes as scanning probe microscopy (SPM) tips has received considerable attention. The experiments to date are non-contact (or tapping) mode experiments that rely on the slender nature of the nanotubes for increased resolution or accuracy. We have also used MD simulations to examine the utility of several types of carbon nanotubes as SPM tips for the study of tribology in contact mode.

4:45 PM Q9.10
CONSEQUENCES OF COMBINED CHEMICAL AND TRIBOLOGICAL STIMULATION OF SINGLE CRYSTAL SURFACES: AN EXAMPLE OF NANOMETER-SCALE TRIBO-CHEMICAL SURFACE MODIFICATION.
Thomas Dickinson, Rizal Hariadi, and Stephen Langford, Physics Department, Washington State University, Pullman, WA.

We have examined the effects of exposing slightly soluble inorganic single crystals to aqueous solutions of a wide range of under- and super-saturations to tribological loading with a scanning probe microscope (SPM) at various normal stresses, tip radii, and lateral velocities. The SPM can be used to monitor the wear or deposition processes. We find well defined conditions for either removal or deposition at atomic (monolayer) steps. These effects are synergistic in the sense that the rates are fastest for particular combinations of these parameters. Crystal structure strongly influences the rates of both removal and growth at steps, showing unique dependencies on the bonding geometries of individual steps. These unique phenomena can be exploited in the production of both atomically flat surfaces and nanometer-dimension surface modification. Extension of this work to polymer surfaces in weak solvents will also be reported. This work is supported in part by the National Science Foundation, ENG/CMS.