SYMPOSIUM U
Mechanical Properties Derived from Nanostructuring Materials
April 22 – 25, 2003

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*Invited paper
SESSION U1: BULK AND STRUCTURAL NANOMATERIALS
Chair: David F. Hailer
Tuesday Morning, April 22, 2003
Metropolitan I (Argent)

8:30 AM U1.1
RECENT RESULTS ON THE DUCTILITY OF NANOCRYSTALINE METALS
Carol Koch, North Carolina State University, Dept of Materials Science and Engineering, Raleigh, NC.

While the hardness and strength of nanocrystalline metals is found to be significantly increased over those of their conventional (micron or larger) grain size counterparts, ductility values have been typically low. For many pure metals prepared by 'two-step' processing which require the consolidation of powder or particulates, the work associated with processing can mask the inherent ductility behavior. More recently, there are several examples of samples prepared by 'one-step' processes such as electrodeposition or severe plastic deformation in which consolidation is not necessary and therefore the possible artifacts associated with it such as porosity or incoherent particle bonding are eliminated. In some materials made by 'one-step' processing, significant ductility has been observed. This talk will review the evidence for ductility results for nanocrystallized metals and alloys and suggest reasons for the large variability observed for this property. Experiments from the authors laboratory and from the literature will be presented.

9:00 AM U1.2
SUPERPLASTIC BEHAVIOUR IN NANOCRYSTALLINE ELECTRODEPOSITED Ni AT 600K F. Dalla Torre and H. Van Suggeren, Paul Scherrer Institute, Villigen PSI, Switzerland; U. Victoria, Basin Technology CRPP-EFPL, Villigen PSI, Switzerland.

Tensile properties of nanocrystalline electrodeposited Ni with a mean grain size of 22nm are measured at different temperatures ranging from room temperature up to 600K. The mechanical properties are accompanied by careful structural analysis by means of XRD and TEM at room temperature a ligament plasticity is obtained. Measurements of activation volume and strain rate sensitivity indicate that, for values obtained for coarse grained Ni, dislocation activity is very limited but grain boundary accommodation mechanisms are not fully operative neither. At 600K however, the material behaves superplastically. It will be shown that this can be attributed to the presence of a second Ni-S phase in the grain boundaries that is forming in situ during annealing and deformation. The second phase has a low melting temperate and therefore plays a lubricating role for the grain boundaries [Acta Mater. 2002].

9:15 AM U1.3
STRUCTURAL EVOLUTION OF NANOLAMINATES DURING SEVERE PLASTIC DEFORMATION: MOLECULAR SIMULATIONS IN THE CO-ZR SYSTEM. Alan C. Land and Christopher A. Eckert, Department of Materials Science and Engineering, Massachusetts Institute of Technology.

Plastic deformation is commonly used to prepare unique nanoscale structures with well-defined mechanical properties, for example by ball milling, equal-channel angular extrusion, or high-pressure torsion. One such method, employing repeated folding and rolling of elemental foils, can produce laminate structures with layer thicknesses on the nanoscale. Further plastic straining of such nanolaminates has also been shown to produce amorphous alloys, although there is little understanding of the nanoscale mechanisms behind this amorphization. In the present work, we explore the final stages of such a mechanical alloying process via molecular simulations. Initial CO-Zr nanolaminates are sequentially strained and consolidated, and the amorphization process is followed through the evolution of the atomic radial distribution functions. The results are in qualitative agreement with existing experimental data, and provide insights into experimentally inaccessible features of the structural evolution.

9:30 AM U1.4
NANOINDENTATION TESTS ON HIGHLY ORIENTED PYROLYTIC GRAPHITE (HOPG) Chien-Hsun Xu and Tong-Yi Zheng, Hong Kong University of Science and Technology, Department of Mechanical Engineering, Clear Water Bay, Kowloon, HONG KONG.

Nanoindentation Tests were conducted on Highly Oriented Pyrolytic Graphite and the morphology of the impression was examined by scanning electron microscopy. The nanoindentation loading curves reveal a pop-in and multihop pop-in phenomena, which is induced by fracture of the graphite layers and/or by delamination between the layers. From the load at pop-in, we can estimate the fracture strength of the layers and/or the bonding strength between the layers. Internal force microscopy pictures show that the nanoindentation test result in steps at the atomic flat surface and the step density near the impression caused by large indentation loads is obviously higher than the density with small loads. It was observed that the nanoindentation test cause the formation of carbon tubes, which are rolled up by the delaminated graphite layers.

10:15 AM U1.5
NANOMECHANICS OF CERAMIC-BASED MATERIALS: ISSUES OF SCALE Brian R. Loomis, Antonia Fajaras, Heryl Chia, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

The role of characteristic dimension in the mechanical response of ceramic-based materials is addressed, in special relation to crack initiation and propagation. Specific issues considered include: contact dimension, flaw size and microstructural scale (monolithic materials); and coating thickness (layer structures). Fundamental brittle-ductile transitions in behavior as these characteristic dimensions diminish through the microscopic to the nanoscopic will be examined. Implications of these transitions in relation to strength, toughness, brittleness, fatigue and wear will be discussed.

10:30 AM U1.6
CREED BEHAVIOUR OF A CRYSTALLIZED Si-B-C-N CERAMIC OBTAINED FROM THE PRECURSOR T3-1 ([B12C12H12][Si4N4]). Himi Kishita, N. V. Andre Zimmermann, Fritz Aldinger, Max-Planck-Institut für Metallforschung and Institute for Niemittallische Anorganische Materialien, Universität Stuttgart, Polymetallurgisches Laboratorium, Stuttgart, GERMANY.

Boron modified silicon carbides, hereafter referred to as Si-B-C-N ceramics, are new class of high temperature materials which offer very interesting properties at elevated temperatures. In applications such as gas turbine industries and in nuclear power applications such as reactor cores, where a combination of high temperature and low stresses can cause the material to irreversibly deform as a function of time, materials having good creep resistance are required. With respect to this, Si-B-C-N ceramics offer a great potential. Anomalous Si-B-C-N ceramics obtained from the solid state thermodynamics of organic precursors have been investigated earlier. They exhibited very good creep resistance, oxidation resistance and thermal stability at elevated temperatures compared to conventionally sintered materials due to the lack of low melting point oxide grain boundary phases. Since amorphous materials are metastable, devitrification takes place at high temperatures and nano-crystallites of SiC and Si3N4 are formed in situ in the amorphous material beyond 1700°C. It seemed therefore interesting investigating whether the creep rate could be further reduced by devitrification of the amorphous state. The polymer precursor boron modified poly(vinylidene) denoted as T3-1 with the chemical composition ([B12C12H12][Si4N4]) was melted and sieved. The polymer particles from different size fraction were compacted using a graphite die in a uniaxial warm pressing machine at a pressure of 300 MPa and in the temperature range 550°C to 350°C. The green bodies were pyrolysed in an argon atmosphere at a temperature of 1300°C where the organic polymer converts into an inorganic amorphous ceramics. These amorphous ceramics were annealed under various conditions of temperature, nitrogen pressure, overpressure and holding times and nanocrystalline Si-B-C-N ceramics were produced.

Compression creep experiments were carried out in atmospheric pressure on nano-crystalline Si-B-C-N ceramics at loads varying from 5-100 MPa and in the temperature range 1350°C -1500°C to investigate the high temperature deformation behavior of the material. The interest is to understand the mechanism of deformation in these nano-crystalline Si-B-C-N ceramics at elevated temperatures and to compare the results with that of amorphous ceramics. The investigation also includes the determination of the viscosity of the material at high temperatures and also comments on the mechanical behavior.

10:45 AM U1.7
FRACURE TOUGHNESS OF NANOCRYSTALLINE Li2 [Al4-x, x=1.4+XAT% Mn]3Ti PREPARED BY MECHANICAL ALLOYING AND CONSOLIDATED BY SPS. Hee Sup Jung, Hwan Qyun Moon, Sung Hoon Lee, Seon Jin Kim, Division of Materials Science and Engineering, Hanyang University, Seoul, SOUTH KOREA.

The modification of the chemical composition of trivalent oxides by alloying with substitutional elements such as Cr, Mn, Fe, Co, Ni, Cu and Zn may result in higher density and fracture toughness. Mechanical alloying was conducted with [Al4-x, x=9.5%]Ti [x=0-12.1]powders and the Li4.13 structure was formed only in the Mn concentration of 8-12wt %. The SPS (spark plasma sintering) process was conducted to sinter nanocrystalline Li2 [Al4-x, x=1.4+XAT% Mn]3Ti and it was achieved to 99% of relative density, without sintering shrinkage. In binary Al4Ti, the final sintering temperature was 864°C, which was
further reduced to 68°C by the addition of 12% H₂O. The micro-hardness test, grain size measurements, and fracture toughness test were also conducted on the same samples. With increasing temperature, micro-hardness decreased by heterogeneous segregations of Al₂O₃, Al₃O₅, and TiC, while fracture toughness increased. The Vickers indentation fracture toughness of compacts was also investigated. Fracture toughness decreased as Mn content increased. The lowest fracture toughness (1.15MPa m¹/² under 1kg load) was measured at 12% H₂O. According to the results obtained from the microstructure, fracture toughness and grain size studies of (Al₆X₆-Nb)₂NC nanocomposites, it may be considered as adequate for high temperature structural applications.

11:00 AM U1.8
EXPERIMENTAL GRAPHITE NANOPlatelets AS REINFORCEMENTS FOR POLYMERS. Lawrence T. Deen and Hiyokumi Fukushima, Department of Chemical Engineering and Materials Science and Composite Materials and Structures Center, Michigan State University, East Lansing, MI.

Nanocomposites composed of polymers reinforced with reinforcements of less than 100 nm in size, are being considered for applications such as interior and exterior necessary for automobiles, structural components for portable electronic devices, and films for food packaging. While most nanocomposite research has focused on exfoliated clay platelets, the same nanoreinforcement concept can be applied to other layered material, graphite, to produce nanoplatelets and nanocomposites. Graphite is the stiffest material found in nature [Young's Modulus = 300 GPa], having a modulus several times that of clay, but also having excellent electrical and thermal conductivity. Surface treatment, exfoliation and dispersion in a matrix polymer results in a composite with excellent mechanical properties as well as electrical properties, opening up a new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are requirements as well. In this paper, the mechanical properties of an exfoliated graphite reinforced epoxy composite will be presented, including modulus, strength, coefficient of thermal expansion, as well as electrical and thermal properties. The results will be compared and contrasted with the same epoxy matrix reinforced with nanoycar, vapor grown carbon fibers and particulate graphite. The results show that nanocomposite materials made with these nanoplatelet materials have three times the modulus of nanoclay platelet reinforced composites. With the proper surface treatment of the nanoplatelet, little reduction in composite tensile strength was detected compared to the neat matrix. Impedance measurements have shown that these platelets percolate at below 3 volume percent and exhibit a 10 order of magnitude reduction in impedance at these concentrations.

11:15 AM U1.9
SHEAR-INDUCED MESOSTRUCTURE IN POLYMER-NANOClay NETWORKS. Sheng Lin Gibson, Charles C. Hsu, Erik H. Kibbe, Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland, and Louisiana State University, Department of Chemistry, Baton Rouge, LA; Hong Do Kim, Kyunghee University, Department of Chemistry, Yongin, Kyungkido, KOREA.

The mesoscopic response of a model polymer-nanoclay gel is measured using small-angle neutron scattering, shear light scattering, optical microscopy, and rheometry. When combined in solution with the acid-treated polyethylene oxide, reversible short-range attractive polymer-clay interactions create a dynamic network with ideal clay dispersion that is homogeneous on a macroscopic scale but heterogeneous on the nanometer scale. As the shear distorts the nanoscopic structure and ruptures the network, coupling between composition and stress leads to microscopic phase separation, reminiscent of other shear-induced structural transitions. On much smaller length scales, the platelets exhibit a shear-induced mesoscopic structure, whose surface normal is parallel to the direction of vorticity. We examine similarities with flow-induced transitions in other complex fluids, and we suggest that the clay might orient in response to a basal stress arising from viscous and elastic forces with incommensurate wavelengths, where these domains represent instable remnant ‘droplets’ of the equilibrium gel.

11:30 AM U1.10

Nanolayered metallic composites, synthesized by physical vapor deposition, exhibit nearly fifty-fold increases in hardness when the bilayer periods are on the order of a few to a few tens of nanometers. However, limited work has been done so far to characterize the deformation behavior of these vapor deposited nanolayered composites when subject to large plastic strains. In this presentation, the deformation behavior during cold rolling of deposited Cu-Nb multilayered foils. The development of dislocation substructures, work hardening and eventual fracture of these nanoscale composites is studied as the bilayer thickness varies from micrometers to nanometers. The presentation will highlight how the nanostructured length scales lead to new regimes of plasticity in metals not observed in microscale materials. The nanoscale multilayers exhibit extreme strain stability up to 40% undergoing uniform reduction in layer thickness to high levels of plastic strain. Large reduction in thickness is accomplished without the formation of the classical dislocation cell structures. Furthermore, no out-of-plane lattice rotations are observed. These results suggest that the deformation occurs via a coordinated slip mechanism, in which the interface plays a critical role in the homogeneous distribution of slip. The mechanisms of work hardening, in the absence of the dislocation cell structures, are discussed. Limited deformability is observed at bilayer thicknesses of a few nanometers or less. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

11:45 AM U1.11
INVESTIGATION OF THE SURFACE STRESS IN SiC AND DIAMOND NANocrystals BY IN-SITU HIGH PRESSURE POWDER DIFFRACtion TECHNIQUE. B. Polska, S. Stelmakh, E. Grzebek, S. Gierlotka, High Pressure Center UNIPRESS, Warsaw, POLAND; Y. Zhao, Los Alamos National Laboratory, Los Alamos, NM; W. Polska, USRA/NASA-MSCF, Huntsville, AL.

The real atomic structure of nanocrystals determines key properties of the materials. For such materials the serious experimental problem lies in obtaining sufficiently accurate measurements of the structural parameters of the crystals, since very small crystals constitute a two-phase than a uniform crystallographic phase system. As a result, elastic properties of nanograins may be expected to reflect a dual nature of their structure, with a corresponding set of different elastic properties determined by the structural parameters of the powder diffraction technique. For nanocrystalline, even one-phase materials such measurements are particularly difficult to make since determination of the lattice parameters of very small crystals presents a challenge to standard evaluation of powder diffractograms. In this investigation we used our methodology of the structural analysis, the "apparent lattice parameter" (alp) concept. The methodology allowed us to avoid the problem (if applied to nanocrystalline) of standard powder diffraction evaluation techniques. The experiments were performed for nanocrystalline SiC and GaN powders using synchrotron sources. We applied both hydrostatic and acoustic pressures in the range of up to 40 GPa. Elastic properties of the samples were examined based on the measurements of a change of the lattice parameters with pressure. The results show a dual nature of the mechanical properties (compressibilities) of the materials, indicating a complex, cross-shell structure of the grains.

SESSION U2: THIN FILMS AND MULTILAYERS

1:30 PM U2.1
MECHANICAL BEHAVIOR OF FILMS, NANOPHASES AND NANOCrystalline Materials. William W. Gerberich, John J. Jungk and William M. Moore, University of Minnesota, Chemical Engineering and Materials Science, Minneapolis, MN.

Recent work on Si nanoparticles and various thin films has strongly suggested that work hardening of very small volumes allows one to achieve theoretical strengths. Deformation and strength properties of nanostuctured films, nanospheres and nanolumps as processed by sputtering, lithography and scribing will be presented. For FCC, BCC and HCP nanocrystalline structures of Au, Ta and Ti, it will be shown that the true strain to strengthening is controlled by both microstructure and constraint. Free surface conditions, as modified by atomic layer deposition (ALD) are examined as well. The goal is to understand how image and evoloduced dislocation arrangements contribute to the strengthening of processed features in the 20 to 200 nm scale regime. With 2 to 20 nm overlayers of ALD-processed amorphous Alumina, differences in flow strength on the basis of surface constraint will be examined.

2:00 PM U2.2
SYNTHETIC AND MECHANICAL PROPERTIES OF TiN/AlN THIN FILM HETEROSTRUCTURES. Cindy Waters, Dhirajny Kumar, Sergey Yermchenko, Zhiqiang Xu, Jag Sunkar, NSF Center for Advanced Materials and Smart Structures North Carolina A&T State University, Greensboro, NC.
There is a growing research interest in TiN and AlN due to their promising mechanical, electronic and optoelectronic properties. Our studies have shown that mechanical properties can be improved significantly by forming thin film heterostructures of the two materials. We report on our pulsed laser deposition assisted synthesis, microstructural characterization, and mechanical properties of TiN/AlN multi-layer structures. The TiN/AlN superlattice structures are fabricated on (100) silicon substrates at different temperatures (400-880°C) and different nitrogen ambient pressures. The nanomechanical properties of the different layers were measured with a tip-supported force feedback interferometer. The improvement in the mechanical properties of TiN/AlN heterostructures has been found to be associated with interfacial interaction between layers. The interfacial interaction, in turn, depends on processing parameters the most important among which is substrate temperature.

2:15 PM U2.3

YIELD OF Te₂Ga₂As SUPERLATTICES UNDER NONOINDENTATION AND BENDING. Stephen Lloyd and Bill Clegg, Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UNITED KINGDOM; Ken Ping, Andy Bashly, David Dunstan, Centre for Materials Research, Queen Mary, University of London, London, UNITED KINGDOM.

The coherency strain in InGa1-xAlx superlattices can be continuously varied through control of the In content. Since these structures can be grown with high structural and electronic quality, we have used them to study the effects of coherency strain on yielding. Previous work has shown that these superlattices display a remarkable resistance to the appearance of dislocations even at temperatures above the melting point. Under nonindentation at room temperature the hardness of the superlattices decreases with increasing strain modulations in the layers, while under 2-point bending at 500°C there is a small increase in the yield stress with increasing strain modulation. Here we investigate the contrasting yield behaviour at different temperatures by examining the deformation in each case in the transmission electron microscope. Use of a focused ion beam microscope allows electron transparent sections to be made through specific sites, such as nonindentations. In addition, large areas of uniform thickness can be machined which is useful to examine the deformation of the bent specimens. Initial investigations have shown that twinning accommodates the majority of the plastic strain under room temperature indentation, using a spherical indenter. In this paper we discuss how the yield point, size of plastic zone and twin density and size varies with the strain modulation in order to understand the changes in hardness in these conditions where the dislocation mobility is low. Under bending at high temperature dislocations are much more mobile, hence dislocation sources can be activated to encode the pattern of slip on the surface, and local ‘tearing’ of the superlattice. We also discuss the way in which coherency strain can be relieved through the activation of these dislocation sources in superlattices with a high strain modulation.

2:30 PM U2.4

THICKNESS EFFECTS ON MECHANICAL BEHAVIOR OF ALD FILMS. N.R. Moody, Sandra National Laboratories, Livermore, CA; T.J. List, J.V. Steiner, R.T. Boyce, and T.M. Mayer, Sandia National Laboratories, Albuquerque, NM; S.M. George, University of Colorado, Boulder, CO.

Strength, friction, and wear are dominant factors in the performance and reliability of materials and devices fabricated using microsystem technologies. While adequate for some applications, as-fabricated strength and wear properties severely restrict use of these devices in many dynamic applications. Applying coatings and films is one method to enhance their performance and reliability. This study characterizes films using Atomic Layer Deposition (ALD) as it is ideally suited for applying highly conformal, thin nano-scale films with monolayer precision, necessary for coaxing microsystems devices. Results focus on the mechanical performance of tungsten and aluminum oxide ALD films. The films were deposited to thicknesses ranging from 1 to 200 nm to highlight the evolution of film and substrate contributions. Nonindentation was then used to measure elastic and plastic properties. These tests showed that the measured modulus of both film systems increased with film thickness. In contrast, hardness of the tungsten films increased significantly with film thickness, while hardness of the aluminum oxide decreased just as dramatically. These results will be discussed in terms of composition and structure of the ALD films and their impact on potential applications. This work supported by U.S. DOE.

2:45 PM U2.5

MATERIALS AND GEOMETRY OPTIMIZATION FOR THE DEVELOPMENT OF ULTRA HIGH SENSITIVE NANO-MECHANICAL RESONATORS. Kyung-S. Son, Robert W. Fathauer, Thomas George, Jet Propulsion Laboratory, MSMS Technology Group, Pasadena, CA; Brian H. Houston, Naval Research Laboratory, Washington, D.C.

Due to their ultra small volumes, high sensitivity, and high operating frequencies, nano-mechanical resonators have numerous applications including creation of single atomic force sensing, measurement of quantum mechanics of particles, IF communication and in precision time standards. Among fundamental unresolved scientific issues are the factors that control the intrinsic quality factor (Q) of these resonators, which determines the sensitivity of these devices. Several factors have been reported to influence the Q of resonators including the thermoelastic properties of the resonator material, surface properties, point defect movement etc. However, the dominant loss mechanisms influencing the Q are very poorly understood and subject to considerable debate in the literature. Design at the nanometer scale poses new challenges because some of the continuum assumptions used in conventional models break down and the role of surfaces becomes increasingly important. To end this, we are pursuing a two-pronged effort with modeling and experimental work going hand-in-hand to develop high Q nano-mechanical resonators. We have optimized the geometry of a particular type of resonator known as the double-paddle oscillator and are currently studying the behavior of micron-scale structures. Performance comparisons will be made to micrometer and nanometer-scale resonators with other geometries. Novel materials choices as well as fabrication methods are also key factors for high Q. We have fabricated nano-resonators using nanoscale laser beams and precise control of the component layers very little with In-content, they are a model system to investigate the effects of coherency strain on yielding. Previous work has shown that these superlattices display a remarkable resistance to the appearance of dislocations even at temperatures above the melting point. Under nonindentation at room temperature the hardness of the superlattices decreases with increasing strain modulations in the layers, while under 2-point bending at 500°C there is a small increase in the yield stress with increasing strain modulation. Here we investigate the contrasting yield behaviour at different temperatures by examining the deformation in each case in the transmission electron microscope. Use of a focused ion beam microscope allows electron transparent sections to be made through specific sites, such as nonindentations. In addition, large areas of uniform thickness can be machined which is useful to examine the deformation of the bent specimens. Initial investigations have shown that twinning accommodates the majority of the plastic strain under room temperature indentation, using a spherical indenter. In this paper we discuss how the yield point, size of plastic zone and twin density and size varies with the strain modulation in order to understand the changes in hardness in these conditions where the dislocation mobility is low. Under bending at high temperature dislocations are much more mobile, hence dislocation sources can be activated to encode the pattern of slip on the surface, and local ‘tearing’ of the superlattice. We also discuss the way in which coherency strain can be relieved through the activation of these dislocation sources in superlattices with a high strain modulation.

3:30 PM U2.6


Future technologies will rely on a complex integration of materials and functionality that bridges several length scales to connect nanometer-scale architectures to the real world of man. Part of this vision will be the ability to produce mechanical work at the nanoscale and the transduction of energy and information from nanoscale to macroscopic systems. Since many architectures of the future will be constructed from nanostructured materials, it is essential to understand the mechanics and limits of mechanical deformation and stability as well as the ultimate properties of the nanoscale material. At this size, internal interfaces comprise a significant portion of the material's volume and may have a dominant influence on the material's mechanical properties. This talk will review the development of new materials to achieve novel mechanical properties based upon tailored nanostructures and discuss the current understanding of the mechanisms that govern their mechanical response. Through collaborations within the Center for Integrated Nanotechnologies, we have developed tests to enable characterization for testing the limits of critical strengthening and toughening mechanisms, such as the nano-dispersion or grain-size strengthening of metals and strength modification in metal nanostructured composites. We have found grain-size strengthening in homogeneous Ni follows the classical behavior down to ~15 nm in size, while the strength drops in layered metals below layer thicknesses of ~5 nm for malleable (e.g., Cu-Ni) and below ~1 nm for immalleable systems (e.g., Cu-Ni). Also, we have investigated the effect of variations in density and bonding on the mechanical properties of amorphous systems, such as aluminum and tetrahedrally-bonded carbon, using energy dispersion in small-scale structures. This work was partially supported by the DOE Office of Basic Energy Sciences. Sandia and Los Alamos are multiprogram DOE laboratories operated by Sandia Corporation under contract DE-AC04-94AL85000 and the University of California, respectively.
Understanding bilayer behavior is a critical step in the successful development of ultrahigh-strength nano-layer composites. We have analyzed max/substrate interactions at the interface of Ni/Cu bilayers using plan-view and cross-sectional transmission electron microscopy (TEM). The bilayers consisted of varying thickness of Ni (~200 nm) deposited onto 1500 nm Cu. Conventional electron microscopy was used to determine the interface properties of the bilayers, while high-resolution TEM performed on cross-sectional samples was used to analyze the interface in more detail. It is demonstrated that the interface properties of Ni/Cu bilayers do not exist and are governed by a 2mm x 12nm rectangular window etched through a Si wafer. Creep behavior (stress relaxation) was investigated using the normal and transverse modes of the composite membrane to determine the stress. This method has high sensitivity to stress changes in very thin metal films. Thermal cycling to temperatures up to 300°C was used to establish a stress, and the time dependence of the stress was examined at temperatures between 20 and 100°C. In some cases the time dependence follows a logarithmic expression based on dislocation motion. Results will be presented for Ni, Cu, and Au.

4:30 PM U2.9 FULLY REVERSIBLE DISLOCATION-BASED DEFORMATION IN A NANO LAYED CARBIDE: Ti$_2$SiC$_2$. Michal W. Barczewski, Tejin Zhou, Surya R. Kabidindi, Andrew K. Morgan, and Dean D. Haidas, Dept. of Materials Engineering, Philadelphia, PA, Mikhail Rudnov, Oak Ridge National Laboratory, Oak Ridge, TN.

Without exception, all known crystaline solids exhibit a fairly linear elastic strain response at low stresses. In the elastic regime, the response is reversible and non-dispersive. Once the elastic regime is exceeded, the response is plastic and non-reversible (i.e., the hysteretic loops formed during loading and unloading open). In fact, the only known materials that exhibit fairly large regimes of nonlinear elastic response with significant levels of energy dissipation in fully reversible hysteretic loops are rubbers (which are lightly cross-linked and non-crystalline). In this work, we show that macroscopic polycrystalline Ti$_2$SiC$_2$ cylinders can be compressed, at room temperature, to stresses of up to 1 GPa, and fully recover upon the removal of the load. The stress-strain curves are non-linear, outline fully reversible reproducible closed loops whose size and shape depend on grain size, but not strain rate. We believe, the energy dissipated when cycling to 1 GPa, viz. 0.7 J/m$^2$, is a record for crystalline solids. At temperatures higher than 1000°C, the stress-strain loops are open and the response becomes strain rate dependent. Cyclic hardening is observed at 1200°C, for both fine and coarse-grained samples. This hitherto unreported phenomenon is attributed to the fully reversible formation and annihilation of incipient kink bands at room temperature deformation. At higher temperatures, the incipient kink bands dissociate and coalesce to form regular kink bands that are no longer reversible. The technological implications of having a lightweight, inexpensive, elastically stiff solid, (with a specific stiffness as high as that of Ti) that can be machined with a normal back saw, with compressive strengths of 1 GPa, that also can double a significant portion (~50%) of the mechanical energy will be discussed.
U3.3 ELECTRICAL FIELD MORPHOLOGY CONTROL IN THIN MOSEST NANOCOMPOSITES: MODEL SYSTEMS FOR STRUCTURE-PROPERTY RELATIONSHIPS. Hikari Koerner, University of Dayton Research Institute, Dayton, OH; John D. Jacobs, David W. Tomlin, Nathan A. Forrest, Richard Van, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Low volume additions (1-5%) of highly anisotropic nanoparticles, such as layered silicates or carbon nanotubes, provide property enhancements to the matrix. These are comparable to that achieved by conventional loadings (15-40%) of traditional fillers. The lower loadings facilitate processing and reduce component weight. Critical to all of these endeavors is establishment of scientifically sound structure-property relationships, not just demonstration of analytical descriptions to experimental data. Developing systems with the simultaneous morphological characteristic and control at the micro, millimeter scale necessary for detailed investigation of mechanisms of deformation is a challenge. Here, we use elastic fields of modest strength to align nanoparticles in an uncured epoxy matrix and then lock the orientation by amine crosslinking. The data on nanoparticle orientation opens up new possibilities for investigating mechanical and transport properties at interfaces. We will discuss results on the dynamics of the poling process derived from in situ X-ray experiments. Additional experiments, including TMA and DMA, allow us to evaluate the influence of the reorientation of particle and matrix/interface on macroscopic properties, including thermal coefficient of expansion, tensile strength and dynamic mechanical response.

U3.4 EVIDENCE FOR NEW MODULUS/DENSITY SCALING RELATIONSHIPS AND FRAMEWORK ARCHITECTURES IN POLYMER NANOARCHITECTURES. Hongfan Pan, Sandia National Laboratories, Chemical Synthesis and Nanomaterials Dept, Albuquerque, NM; Christopher Hartshorn, Dept of Chemistry, Univ of New Mexico, Thomas Buchheit, David Tallant, Sandia National Laboratories, Albuquerque, NM; Salvatore Torquato, Princeton Univ, Dept of Chemistry and Princeton Materials Inst, Princeton, NJ; Jeffrey Brinker, Sandia National Laboratories, Chemical Synthesis and Nanomaterials Dept, Albuquerque, NM; The Univ of New Mexico, Fiber Science Center for NanoEngineered Materials and Dept of Chemical and Nuclear Engineering, Albuquerque, NM.

A continuing challenge in the integration of nanomaterials into microsystems is their mechanical behavior. However, much effort has been put on synthesis of nanostructured materials. Little attention has focused on the mechanical performance of synthetic nanostructures. In addition, an important issue in mechanical properties of these structures is the effect of self-assembled nanostructures can be evaluated by mechanical continuum model or not. In this presentation, we developed a unique synthetic route to produce highly periodic nanostructure with controlled porosity and structures scaling with one same recipe. Our results show that these self-assembled nanostructures exhibit structure-specific scaling relationships of modulus and density. For ordered nanostructures [hexagonal and cubic], the relative modulus can exceed the upper bound predicted by continuum mechanics.

Detailed results from nanoindentation, Si-NMR, and Raman spectroscopy will be presented to understand the structure-chemical property relationships and deviations from continuum behavior at molecular level. Sandia National Laboratories, Dratz Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000.

U3.5 GRAIN SIZE EFFECTS ON NANOINDENTATION LOADING BEHAVIOR OF Pt THIN FILMS. Seungmin Hyun and Richard P. Vinci, Lehigh Univ, Bethlehem, PA.

Dislocation behaviors exhibited during depth-sensing indentation of thin films are often very different from those associated with traditional large-scale materials because the deformation field size is often in the range of the microstructural feature size. Although significant deformation behavior has been heavily investigated, the deformation behaviors particular to thin films are still not fully understood. Recently, it has been shown that microstructure plays a key role in determining the magnitude of the pop-in events in Au thin films. A small-grained film and a large-grained film, defined relative to the indenter tip size, displayed very different loading curves. This effect was attributed largely to easy dislocation nucleation when the indenter tip was on the grain boundary. In the present study, microstructure dependent deformation behavior of Pt films was systematically explored to add to the growing understanding of pop-in behavior of polycrystalline materials. A detailed examination of grain size effects on the film was performed by preparing Pt films with different average grain sizes. The deformation behavior was studied in terms of both grain size and proximity of the indenter tip to a grain boundary. Pop-in behavior of Pt films is affected by the proximity of a grain boundary in the indented area. Large scale deformation behaviors (pop-in events) were observed when a single grain was indented whereas fewer pop-in events were observed if an indentation was performed near or on the grain boundary area.

U3.6 CONTINUUM ANALYSIS OF COOPERATIVE PIT ISLAND FORMATION AND STABILITY IN Si/Ge ON Si(100). Ninh Singh, Dalhousie Univ, Nova Scotia, Department of Materials Science and Engineering, Charlottetown, VA.

Recent experimental work [3, 4, 5, 6, 7] has suggested that the cooperative nucleation and growth of pits and islands at pit edges in SiGe/Si(100) epitaxial films. The pits, which are observed to form under certain growth conditions, evolve along with the islands until a complete island is nucleated around the pit. Once formed, the island shows a correspondence to a "Quantum Fortress," exhibits a surprising stability, with no further lateral growth during continued deposition or annealing. The pits comprise of low energy (501) facets (inverted (100) pyramid) and the islands surrounding the pit also exhibit faceting. Elastic finite element analyses of these configurations were carried out to investigate the dependence of strain energy and surface stress on pit/island geometry. In particular, our results provide insight as to the mechanism responsible for the observed size stability of the pit/island structure once it has become fully developed. Surface stress gradients are also found to be responsible for the initial island formation at the center of pit edges rather than at the pit corners during growth.

U3.7 DYNAMIC SCALE FRICTION OF AMORPHOUS HYDROGENATED CARBON THIN FILM IN MEMS. Myeong-Gyu Ko and Jong-Won Park, Department of Nanostructure Semiconductor Engineering, Hanyang University, Seoul, KOREA.

Diamond and diamond related carbon thin film have extensively studied over the past several years due to their unique combination of properties. Especially, hydrogenated diamond carbon (-a-C:H), called diamond like carbon (DLC), is a promising friction reducing coating material for MEMS (microelectromechanical system) applications. The DLC film is prepared by electron cyclotron resonance chemical vapor deposition (ECHCD) employing CH4 and H2 gases. It is deposited by the control of CH4 / H2 gas flow ratio, deposition working pressure, and In-situ thermal treatment temperature. The atomic scale friction behavior, structure and properties of a-C:H film are dependent on the deposition condition, thermal treatment temperature and chemical bonds in films. Atomic-scale friction behavior is analyzed by lateral force microscopy (LFM) mode using microcantilever. Hydrogen and carbon concentrations in a-C:H films were studied by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS) and the structure of these films are also analyzed. In a-C:H film properties are determined by the relative amounts of sp2, sp3 and sp3 bonding between the carbon atoms.

U3.8 STIFFENED POLYSTYRENE IONOMERS NEUTRALIZED WITH MIXTURES OF VARIOUS CATIONS STUDIED BY DYNAMIC AND MECHANICAL AND SMALL-ANGLE X-RAY SCATTERING TECHNIQUES. Ho Seung Jeon and Joon-See Kim, Chosun Univ, Dept of Polymer Science & Engineering, Gwangju, KOREA.

The effects of the addition of mixed cations, i.e. Na+/Ca2+, Ba2+/Ca2+, and Ba2+/Zn2+, to the acid form sulfonated styrene ionomers on their dynamic mechanical properties and morphology were investigated. It was found that the matrix glass transition temperatures did not change with the ratio of the one cation to the other. As expected, however, the ratio of one cation to the other in the mixed cations affected cluster glass transition temperatures significantly. It was also found that the activation energies for the glass transitions for the matrix phase remained constant, while those for the cluster phase changed with the ratio of the two cations. In addition, the position of the SALS peak was found to be affected by the type of cations. From the results obtained above, the decrease in the cluster Tg with increasing the ratio of alkaline earth cations in Na+/Ca2+ and Ba2+/Ca2+ mixtures, were explained on the basis of the considerations of the size, charge, and type of cations, which alter the degree of clustering as well as ion-hopping mechanism.

U3.9 MECHANICAL PROPERTIES OF P(Sc60-TiN) and P(Sc60-Ca-Na), P(Sc60-SSN) and P(Sc60-Ma-Na), AND P(Sc60-TiN) and P(Sc60-SSN) IONOMER HOMOBLENDS. Sung-Hwan Oh and Joon-See Kim,
Three different sets of styrene-based ionomer homoblends containing ca. 5 mol% of ionic repeat units, i.e., poly(styrene-co-sodium isonitrile) (P[St-co-ni]), poly(styrene-co-methacyrylate) (P[St-co-MAN]), ionomer blends, sodium sulfonated polystyrene (P[St-co-SNa])/P[St-co-MAN]), ionomer blends, and P[St-co-TAN]/P[St-co-SNa]) ionomer blends, were prepared and their dynamic mechanical properties investigated. It was observed that with increasing ionic content in the blend of P[St-co-TAN]/P[St-co-SNa]) ionomer, the multiplet of the P[St-co-MAN]) ionomer disrupted initially very rapidly, and the interaction modulus of the ionomer increased dramatically. Again, the ion modulus increased significantly with increasing ionic content. In these two ionomer blend systems, the isocyanate, having two ionic groups per ionomer repeat unit, influenced blends more noticeably than the other two ionomer units, containing only one ionic group per ionomer repeat unit. In the blend system of P[St-co-SNa]/P[St-co-MAN]), as expected, the cluster loss tangent peak shifted to higher temperature, ionic modulus decreased, but the ion plateau extended more with increasing the ratio of the P[St-co-SNa] content. However, it should be mentioned that when the ion contents of the methacrylate and sulfonate ionomers increased to over 6 mol%, at which the cluster phase of the P[St-co-MAN]) ionomers is known to become dominant, compared to the matrix phase, the three loss tangent peaks were observed, which implies that methacrylate-rich and sulfonate-rich phases exist together. This might be due to the high-copolymerization efficiency of the copolymer, that is, with increasing ion content the role of ionic units in random copolymer ionomers becomes more important, compared to the role of host non-ionic units. As a concluding remark, the properties of these three ionomers are significantly dependent on the extent of separating, type of ion groups, and the number of ion groups per repeat unit.

U3.12 HIGH-STRENGTH AND SUPERPLASTICITY OF NANOSTRUCTURED MATERIALS. Vitaly Slepnev, Ioffe Physico-Technical Institute of the Russian Academy of Sciences, St. Petersburg, RUSSIA.

The leading role of grain boundaries in the processes of deformation and fracture for nanostructured materials has made possible to reach their extremely high strength characteristics at low temperatures [1] and to observe superplasticity at high temperatures [2]. Tests were carried out on a number of materials (Ni, Nb, Cu and Cu/Co-zeolite composite, Al-alloy) obtained by multiple equal-channel angular pressing. The temperature range was from liquid-helium temperature up to nanostructure destruction one. Comparison of mechanical characteristics of polycrystals with nano and large-sized grains at liquid-helium temperature showed that the first had more expressive "sorption-effect" which observed in wider temperature and strain-rate ranges. The difference in mechanical behavior under tension and compression for nanocrystals as well as the various impurities influence on yield stresses was detected. The thermal effects at a stress jump observed upon transition of a Ni-sample (or Ni-strip placed closed to the sample) from the superconducting state to the normal state were estimated. At high temperatures the stability of nanostructure in Cu increased by doping of ZrO2 or H2O2 particles. The constant-rate tensile deformation and creep of Al-alloy exhibited superplasticity at temperatures of 600-670 K and relative-strain rate of 10^-2-10^-3 s^-1. The relative axial deformation at fracture was about 20000%. It was shown that, upon tension with a constant strain rate, a steady stage appeared: if true stress and strain were taken into consideration, the stress changed with deformation in accordance with well-known formula \sigma = c \exp(n/\kappa T) with constant coefficients. From this it follows that, upon deformation of nanocrystals under superplasticity conditions, an equilibrium structure is formed, which remains unchanged even after long-term deformation. References. 1. V.V. Slepnev, V.I. Nikoiev, B.I. Smirnov, A.B. Lobelev, V.I. Kopjov. Physics of the Solid State. 42, 6, 2015-2020 (2015). 2. M.M. Maksyutov, V.V. Slepnev, M.M. Kamalov. Physics of the Solid States. 43, 11, 2014-2014 (2011).

U3.13 THERMAL ORDERED MESOPOROUS SILICA UNDER COMPRESSION STRESS. Francesco Di Renzo, Anne Galamrez, Helene Camhon, Francois Pajot, Enescu-CNRS, Lipo Matériaux Catalytiques, Montpellier, FRANCE.

Which is the lowest scale at which classical mechanical models for cellular materials can be applied? The narrow distributions of pore size and wall thickness of micelle templated silica at the nanometer scale provide ideal benchmarks for the evaluation of mechanical models. Stress/strain relationships under uniaxial compression have been determined for ordered mesoporous silica with different structures [MCM-41, MCM-48, SBA-15]. A model of sphere bed has been used to correlate the effective elastic properties of the samples. The effects of mesopore topology, secondary microporosity and secondary mesoporosity have been taken into account.

U3.14 NanoMechanical Characterization of Bone. Thorsten Decleer, Eve Dommely*, Marjolein CH. van der Meulen*, and Stephanie Blake, Department of Materials Science and Engineering, Cornell University, Bard Hall, Ithaca, NY. "Department of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY.

Bone is a complex natural composite showing a lamellar structure on the micro scale. In this study, scanning nanindentation was used to access the mechanical properties of single lamellar and inter-lamellar trabecular bone. Only the combination of a careful sample preparation, metrological characterization of the sample surface, and a scanning nanindenter proved to be able to provide an insight into individual mechanical properties of the lamellar structures. The results of quasi-static as well as dynamic nanoindentation tests of bone will be reported and discussed. The dynamic measurements covered a frequency range of 10-220 Hz. By careful surface preparation, we were able to achieve a surface roughness of about 18-20 nm RMS on a lateral scale of about 10 micrometers. Nonetheless, this mandates indentation depths in the range of 100 nm, and above in order to minimize the effect of topography on the measurements. This recalescence conflict with the need to keep the probed volume small enough to sample only one component at a time. A simple volume averaging model was developed and used as a tool to determine when individual lamellar bone structures were being probed and to help determine the properties of the lamellar and interlamellar lamellar links.
U3.15 NONAIDENTIFICATION CHARACTERIZATION OF LASER MODIFIED A319A ALLOY COMPOSITE SURFACE LAYER, S. Nagy*, G.M. Pharr*, A. Lauri Rieser* and Narendra B. Dukhote*,
*University of Tennessee, Knoxville, TN; **Oak Ridge National Lab, Oak Ridge, TN.

In this work, A319Al alloy has been modified by laser on the surface. Microstructure and nanoindentation were carried out on these samples. Microstructures indicate extreme refinement in laser surface melted region. Initial cell size of as-received A319Al alloys was 50 μm whereas the laser treated sample had a cell size of α 230 μm. Nanoindentation was carried out to evaluate the property of local volumes. Average hardness of the laser treated samples showed an increment [1.25 GPa] over that of as-received A319Al (1.1 GPa). The large standard deviation associated with A319Al [5%] was reduced to 2%. The hardness and elastic modulus values (derived from the continuously measured stiffness) were analyzed to investigate size effect from a 'contact' perspective. Also, the unloading load vs. displacement data were curve fitted to power law. The elastic and plastic behavior of the laser modified sample was compared with that of A1 and Si to correlate structure and properties of the laser treated composite material.

U3.16 GRAIN BOUNDARY CHARACTERIZATION AND SLIDING OF [0001] SYMMETRIC TILT BOUNDARIES IN AlMgCu
Katsuyuki Matsunaga, The Univ of Tokyo, Engineering Research Institute, Tokyo, JAPAN; Hitoshi Nishimura, The Univ of Tokyo, Dept of Materials Science, Tokyo, JAPAN; Hirokiy Muto, Toyohashi Univ of Technology, Dept of Materials Science, Toyohashi, Aichi, JAPAN; Takahito Yamamoto, The Univ of Tokyo, Dept of Advanced Materials Science, Tokyo, JAPAN; Yuichi Ishihara, The Univ of Tokyo, Engineering Research Institute, Tokyo, JAPAN.

Aluminium bicrystals with [0001] symmetric tilt grain boundaries were fabricated by diffusion bonding at 550°C in air, and their atomic structures were studied using high resolution electron microscopy (HREM) and static lattice calculations. In order to examine the behavior of grain boundary sliding, compressive creep tests were performed at 450°C using the bicrystal. HREM observations showed that several grain boundaries studied here have symmetric atomic arrangements with respect to grain boundary planes. The creep curves were found to exhibit different profiles depending on grain boundary character, which indicates that grain boundary structures are important for grain boundary sliding.

U3.17 DEVELOPMENT OF A NONSTRUCTURED FERRITIC ALLOY [NFA], Matthew J. Alinger, G. Robert Odette, University of California, Materials Department, Santa Barbara, CA.

Iron powders containing ~14%Cr and smaller amounts of W and Ti can be mechanically alloyed (MA), consolidated and heat treated to produce very high densities of Y2O3 particles and /or coherent solute clusters embedded in Y, O and Ti along with nano-scale grains. These alloys manifest very high strength (static and creep) and corrosion-oxidation resistance up to temperatures well in excess of 700°C. As processed, room temperature Vickers hardness of the powder is as high as ~15 GPa. The nanostructures are remarkably stable, with room temperature Vickers hardness values up to ~745 dph after heat treatment or consolidation by HIP processing at temperatures of 1150°C. The recrystallization temperatures are about 1300°C. Other salient microstructural characteristics of these alloys include discontinuous substructures, residual porosity following consolidation, as well as additional porosity that develops during high temperature heat treatments. The mechanical properties of both the micro- and nano-structures that varies from stage of stage of mechanical alloying, consolidation and heat treatment are characterized by a combination of techniques including XRD, SANS, TEM, atom probe, microhardness and several other complementary methods. The effects of the alloy composition MA milling parameters and consolidation path on these evolutions are examined Tensile and fracture toughness properties of selected alloys are also presented. These observations are used to guide model of the underlying thermo-mechanical processes that mediate the micro- and nano-structure formation and evolution and stability as well as their corresponding effects on key mechanical properties.

SESSION U4: TESTING NANOSCALE MATERIALS
Chair: William W. Gerberich and Jeffrey N. Florando
Wednesday Morning, April 23, 2003 Metropolitan I (Argent)

8:30 AM U4.1 MICROSCALE TENSILE TESTING AND MODELING OF MECHANICAL BEHAVIOR IN NANOSTYLLINE METALS, K.J. Henken, En Ms, and J.F. Molinari, Johns Hopkins University, Dept. of Mechanical Engineering and Materials Science and Engineering, Baltimore, MD.

The reliability of next-generation MEMS, NEMS, magnetic and ultrathin films, and micro/nano devices, in general, will be closely tied to their mechanical performance. To be truly predictive, a fundamental description of the mechanical behavior of these structures must be based on a solid understanding of operative deformation mechanisms, but many of the plasticity models that were developed to describe conventional materials are known to break down at or near the nanoscale. The overarching intellectual challenge of the work described in this talk is to develop a science based methodology for measuring, describing and modeling deformation and fracture processes at or near nanometer length scales. Recent efforts at developing microsample tensile testing techniques, which afford us the opportunity to characterize smallscale and highly scale-specific properties, will be described. Results of ongoing efforts to characterize the tensile strength of nanocrystalline microsamples will be presented, and transient microsample experiments designed to uncover and characterize the dominant deformation mechanisms will be outlined. Preliminary results of finite element (FE) calculations, containing physical models that are based on experimental findings and incorporating cohesive elements with atomistic descriptions of grain boundaries in nanocrystalline materials, will be presented and used to model the collective microscopic response of a compilation of nanocrystalline grains. The support of National Science Foundation (Grant No. DMR0212925) is gratefully acknowledged.

9:00 AM U4.2 MECHANICAL TESTING OF MICRO-SIZE SAMPLES IN UNIAXIAL COMPRESSION, M.D. Ueda, D.M. Dimiduk, Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson AFB, OH; J.N. Florando, Lawrence Livermore National Laboratory, Livermore, CA; W.D. Nix, Stanford University Department of Materials Science and Engineering, Stanford, CA.

In this study we present a general methodology to conduct uniaxial compression experiment on micro-size samples i.e., specimen having a diameter on the order of a few microns-where these samples have been fabricated from a bulk quantity of material (which has been made by an arbitrary process). By shrinking the size scale of the conventional uniaxial compression test, we now have a method to explore specimen size effects at micrometer-length scales for bulk materials. This method also has the potential to allow for the characterization of the single-crystal constitutive response from a single grain/micro-constituent of a polycrystalline/polycrystalline material. Specifically, we demonstrate how to use a Focused Ion Beam (FIB) to machine micro-scale mechanical test specimens into the surface of a material, where the test structures can range in size from single grains to tens of microns in diameter. The mechanical properties of these samples can be measured in uniaxial compression using a microindenter fitted with a flat-ended tip. We present data from small sample experiments conducted on a single-crystal elemental metal (Ni) as well as single-crystal intermetallic alloy (NiAl), and we compare these data with tests conducted on conventional sized samples.

9:15 AM U4.3 COPPER THIN FILM MECHANICAL CHARACTERIZATION BY TENSILE AND INDENTATION TESTING, David Read and Roy Geiss, National Institute of Standards and Technology, Boulder, CO; Richard Emsly, Components Research, Intel Corporation, Chandler, AZ; Guanghui Xu and Tracey Scherban, Technology Development Quality and Reliability, Intel Corporation, Hillsboro, OR.

The mechanical properties of sputtered and electroplated copper films were investigated by microtensile testing of freestanding films and nanindentation of supported films. Microtensile specimens with gauge lengths of 190 micrometers and widths of 7 to 20 micrometers were fabricated using a lithographic process. Some samples were annealed before being tested. Tensile elongation to failure ranged from close to zero to a maximum value of about 0.08. Despite this relatively limited tensile ductility, scanning electron microscopy (SEM) observations of the fracture surfaces indicate locally ductile behavior in both sputtered and electroplated films. The yield strength and tensile strength of the sputtered film are nearly twice that of the electroplated film, due largely to differences. The elastic modulus obtained from microtensile measurements is about half that derived from nanindentation. Low tensile modulus in thin films have been previously reported, with possible explanations including film anelasticity and crack opening and closing at grain boundaries.
Nanoscale studies were conducted on the dynamic behavior of individual nanoparticle chain aggregates (NCA) and their networks. For this purpose, a novel device was fabricated to apply tension to NCAs under controllable conditions. The device is composed of a specimen support and a cartridge. The specimen support is a deformable alloy disc with a narrow slit across which the NCA is deposited; the cartridge is used to connect the specimen support to a specimen elongation support holder. The aggregates were stretched using the specimen holder to widen or narrow the slit gap at speeds from 0.5 to 3000 nm/s, and the motion was observed with a transmission electron microscope. Most of the studies were conducted with carbon NCA (primary particle size 11 ÷ 16 nm) generated by laser ablation of a graphite target. The aggregates were deposited on the specimen support (disc) to form bridges across the slit. When tension was applied, the NCA remained attached to the slit edges. The chains stretched because kinks on the scale of a few particle diameters were straightened by rotation and/or grain boundary sliding at particle-particle interfaces. After the chain became taut, increasing tension produced little additional extension. Eventually, the chain broke and the elastically strained portions along the NCA recovered. This led to fast contraction of the two broken ends. In one of the cases studied in detail, a small primary particle in the chain doubled in length before the chain broke at this location, which occurred because of the high tensile stress in the small particle. In a separate set of experiments, a network of carbon NCA was produced by increased deposition across the slit of a specimen support. Chains in the network broke as they slid in a direction perpendicular to the chains broke midway and not at the junctions with other chains. They rapidly contracted in a way similar to that of the individual aggregates. Applications to the behavior of nanocomposite materials composed of blends of NCA and molecular polymers (e.g., rubber) are discussed.

10:15 AM U4.5
AN IN-SITU TEM NANOINDENTER SYSTEM FOR DEFORMATION STUDIES OF SUB-MICRON WIRES. M. S. Bohji and J.B. Pethica, Univ. of Oxford, Dept. of Materials, Oxford, UNITED KINGDOM; B.J. Inkson, Univ. of Sheffield, Dept. of Engineering Materials, Sheffield, UNITED KINGDOM.

To quantify the mechanical properties of sub-micron wires, an in-situ nanoindenter system is being developed for Transmission Electron Microscope. This miniature displacement controlled nanoindenter will fit inside a side entry specimen holder. The displacements are generated by means of a tube piezo and the force is measured using a fibre optic interferometer. The force-sensing element is a specially designed and manufactured single-walled C60-Buckminsterfullerene encapsulated in a 3-axis inertial positioner has been developed. This positioner has a range of 5 nm with a 300 nm resolution. The system is being used to investigate the deformation of Cu, Al and Ti nano wires under W contact. The indenter is made usingFocused Ion Beam microscope and the tungsten tip is polished electrochemically.

10:30 AM U4.6
MEASURING AND OBSERVING THE INDENTATION BEHAVIOR OF SILICON THRU IN SITU NANOINDENTATION IN A TEM. A. M. Minor and E.T. Lilleyden, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, E.A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; M. Jin and J.W. Morris, Jr., Dept. of Materials Science and Engineering, University of California, Berkeley, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

We present real-time observations of nanoindentation into silicon, which show extensive dislocation-based plasticity at room temperature. Upon unloading, the plastically deformed volume leads to a residual stress that can induce non-cratological fracture. These results can be explained in part by the unique wedge geometry of the samples used. The silicon wedge samples were fabricated through bulk micromachining into wedges that are terminated by a plateau of either 20 or 150 nm. When compared to conventional indentation in TEM, these wafers allow different stress state underneath the indenter. A method for extracting quantitative load vs. displacement data from the voltages-controlled in situ nanoindentation experiments will be discussed. FEM analysis of the wedge geometry and asperity shape dependence of indentation force-displacement data is also used in support of the in situ nanoindentation experiments. Combining all of these techniques, the deformation mechanisms in silicon will be discussed in terms of the competition between dislocation nucleation and phase transformation during the initial stages of indentation.

10:45 AM U4.7
SURFACE MECHANICAL PROPERTY DETERMINATION OF SOFT MATERIALS THROUGH AN AFM NANOINDENTATION EXPERIMENT. Olivier Noel, Maurice Broglio, Gilles Castelain and Jacques Schultz, Université de Haute Alsace et Institut de la Chimie des Surfaces et Interfaces (ICM), Mulhouse, FRANCE.

Atomic Force Microscopy (AFM) gives the opportunity to perform nanoindentation experiments. This technique has been used to probe model cross-linked polydimethylsiloxane networks (PDMS) in order to extract their surface mechanical properties. Nanoindentation Young modulus have been determined and lies over two decades. In order to obtain quantitative measurements with the AFM, systematic studies have been performed (preferentially based on model systems) so that this technique can be used to determine Young modulus of polymeric materials. Especially the radius of curvature has been determined by performing a nanoindentation experiment on a model soft material. A discussion about the difficulties to find out mechanical properties of soft materials is proposed. In particular Young moduli of each sample have been calculated by using different contact mechanics theories (Hertz and JKR theories) and a power law expression. A comparison with the macroscopic moduli has shown that the contribution of the adhesion cannot be neglected on the nanoscopic scale. Consequently, the influence of the indentation depth and, of the contact time between the probe and the sample, has been studied. From then on, the contact mechanics relationships (which depend on the geometry of the indentation) were used to calculate micro indentation experiments (Vicker's tip) were also performed and compared with the others results. At the end, we hope to propose you a finite element simulation (using Castem software) of an AFM nanoindentation experiment (present, still under elaboration) that includes the adhesive and viscoelastic behaviours of the material, as well as the effect of an loading-unloading cycle of the tip.

11:00 AM U4.8
ANALYSES OF THE ELASTIC MODULUS OF A THIN POLYMERIC FILM. Soline Roche, Sandrine Bec, Jean-Luc Loubet, Ecole Centrale de Lyon, Laboratoire de Tribologie et Dynamique des Systèmes, FRANCE.

This paper discusses the interaction between mechanical properties of a thin layer and its substrate. The underlined questions are how the substrates mechanical properties affect those of the film, how the layer's thickness affects its mechanical properties. Nanoindentation tests are performed on polymer films of different layer thicknesses laid on a silica substrate. The mechanical response corresponds to those of the substrate and the film taken as a simple whole. Our aim is to understand the elastic behaviour of the film inside this structure. Modelisations are used to estimate the elastic modulus of the film apart of the global value measured. A comparison of the different literature's models is proposed for layers thicknesses, which are “compliant” applied on “hard” substrates, an increase of the film elastic modulus along indentation is observed. We attribute this increase to an “elastic” effect, taking the dependency of buckling of thin elastic films on the compressive pressure of the substrate and the load during the compression of the film. The relevant experimental parameters governing the phenomenon are pointed out: the ratio between the film thickness and the contact radius, the ratio between the substrate hardness and the film modulus, the experimental temperature in front of the glass transition temperature. In conclusion, some rules are proposed to understand specific behaviour of nanometric layer.

11:15 AM U4.9
INCREASING INITIAL YIELD STRESS AT SMALL LENGTH SCALES. I. Spary, A.J. Bashshy, N M J Bennett, and G M Phillips; Centre for Materials Research, Queen Mary, University of London, UNITED KINGDOM.

Material science projects have used experiments to obtain plasticity size effects in ductile metals. In these experiments indentation stress-strain curves were generated using spherical indenters with radii ranging from a few micrometers to several hundred micrometres and these were compared to data from conventional universal testing. Large radius indenters produced a single indentation stress-strain curve independent of indenter geometry. A power law hardening coefficient equivalent to that in the compression
tests. However, for smaller indenters the indentation stress-strain curves appeared at progressively higher pressures for smaller radius indenters. In this paper we model these experiments using finite element analysis methods. By inputting the uniaxial stress-strain data to the model (effectively, using von Mises criterion) the indentation stress-strain curves for the micro size indenters are reproduced.

However, there is no length scale for the size of indenter. We show that by offsetting the compression stress-strain curve by increasing the initial yield stress and inputting this data to the model, the indentation behaviour of the smaller radius indenters can be modelled. The increase in yield stress with decreasing indenter radius is demonstrated for Cu, W and Ir and is shown to be consistent with the intuition of yielding over a finite volume.

11:30 AM U4.10
ON THE RELATION BETWEEN THE INDENTER SIZE AND THE GRAIN SIZE. RESULTS FROM ATOMIC SIMULATIONS.
A. Honkonen, D. Fechtinger, P. M. Darke, H. Van Steenbergen, Paul Scherrer Institut, Villigen-PSI, SWITZERLAND.

Atomatic studies of nanoindentations have been performed on nanocrystalline samples with different mean grain sizes (6 and 12nm) and single crystal samples, in order to study the influence of the microstructure on the mechanism responsible for dislocation nucleation during displacement controlled indentation. A hard sphere indenter applied to a thin film geometry with an infinitely hard substrate is used and the simulations are done using molecular dynamics and conjugate gradient techniques. The size effect due to the relation between indenter size and grain size is discussed: for the same indentation load, differences in the indentation stress-strain curves are found when the indentation is contained within one grain or when smaller grain sizes, the indentation covers different grains. Careful examination of the activity under the indenter shows that (1) the GB act as sinks for dislocations emitted under the indenter (2) collective motion of grains pointing towards the presence of GB sliding (Phys. Rev. B, 2013).

11:45 AM U4.11
ON THE DECOUPLING OF CHEMICAL AND MECHANICAL SURFACE CONTRIBUTIONS IN A FORCE-DISTANCE CURVE MEASURED BY AFM ON MODEL POLYMERS.
Maurice Brogley, Olivier Noel, Gilles Castéja, Jacques Schultz.

The Atomic Force Microscope (AFM) is a promising device for the investigation of materials surface properties at the nanoscale. Precise analysis of these mechanical properties and in particular, of model surface polymer can be achieved with a nanometer probe. The purpose of this study is to dissociate the different contributions (adhesive and mechanical) included in an AFM force-distance curve in order to establish relationships between viscoelastic properties of the bulk, of the surface and the adhesive forces. Indeed we are interested in the measurements of local attractive or adhesive forces in AFM contact mode, of controlled chemical and mechanical model substrates. Considering that the main technical uncertainties have been listed and minimized, surface force measurements are performed on chemically modified silicon substrates [grafted with hydroxyl, amine, methyl] and elastic functional groups. The results show that the contribution of the surface chemistry (in particular in hydrophobic features) is dominating in the measurement of the adhesion force. In order to investigate the effects of mechanical or viscoelastic contributions, we achieved force measurements on model polymer networks, whose surfaces are chemically controlled with the same functional groups as before (silicon substrates). Young moduli have been determined and lies over two decades. The results show that the viscoelastic contribution is dominating in the adhesion force measurement. At the end, we propose an original relationship (derived from the Gent and Schultz law), which express the local adhesion force to the dissipation energy in the contact and the surface properties of the material (thermodynamic work of adhesion).

SESSION U5. NANOSTRUCTURED MATERIALS IN 1, 2 AND 3 DIMENSIONS
Chair: Kasim Y. Yildiz, Chair and Christopher L. Muilstein
Wednesday, April 23, 2013
Metropolitan I (Argenta)

1:30 PM U5.3
THERMOMECHANICAL BEHAVIOR OF DIFFERENT TEXTURE COMPONENTS IN THIN FCC METAL FILMS.
Shefford P. Baker, Cornell University, Department of Materials Science and Engineering, Ithaca, NY, NY.

Thin metal films are used in a wide variety of nanofabricated devices and are often found to support very large stresses due to differential thermal expansion between the film and the substrates to which they are attached. These stresses are often studied by deducing the relative stress in a film from the curvature that it induces in the substrate. Using x-ray diffraction measurements, we have measured the thermomechanical behavior of crystallographic textures of Ag, Cu, [111] and [100] oriented polycrystalline Cu and Ag thin films. These orientations are found to behave very differently from one another, and from the average behavior determined from subgrain curvature measurements; although the average behavior can sometimes be described as a volume average of the individual texture components. The stress level in [111] orientations can be several times those in [100] orientations, a significantly larger difference than predicted by the orientation factor. The [100] orientations, by contrast, show relatively little strain hardening and stress levels that are insensitive to the film thickness. Large Bragg-like early yielding effects were found in both the [111] and [100] orientations. Understanding these behaviors is critical as film reliability is determined by peak stresses, not averaged stresses. Mechanisms based on dislocation motion and interactions, and on sliding at the film/substrate interface are developed to explain the observed phenomena.

2:00 PM U5.2
NANOINDENTATION OF POROUS Low-K POLYMER FILMS.
Manuel Luis B. Palarin, Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN; Guanghua Xu, Tracey Scherban, Intel Corporation, Hillsboro, OR; Brad Sun, Intel Corporation; Santa Clara, CA; William W. Gerberich, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

The indentation response of thin porous polymer films on silicon substrates was investigated by nanoindentation. Films with 20 and 35% porosities were examined using a Berkovich tip and compared with the nonporous variant. The elastic modulus was found to decrease by as much as 40% when porosity is introduced. A change in slope in the load-displacement curve was observed after reaching a certain load, indicating that partial pore closure is achieved once the depth is beyond half of the film's thickness. The temperature dependence of the modulus was also examined, and was found to exhibit Arrhenius-type dependence. A modeling approach, originally developed for a linear elastic case, is extended to account for pore deformation. Its predictions closely approximate experimental moduli from indentation.

2:15 PM U5.3
ELASTIC PROPERTIES OF LITHOGRAPHICALLY PREPARED NONSTOICHIOMETRIC SILICON NITRIDE FILMS.
Ryan Hartshorn, Alexander Kudlik, Alesie P. Sokolov, Dept. of Polymer Science, Univ Akron, Akron, OH; Arjun P. Mahorovitz, IBM, TJ Watson Research Center, Yorktown Heights, NY; Wen-li Wu, and Christopher L. Seile, NIST Polymers Div, Gaithersburg, MD.

In the semiconductor industry, it is critical to understand how nanostructuring changes the physical properties of materials appropriately from their bulk values. For example, deep UV lithography is used to print the latest image of a structure into a thin photoresist film. An aqueous solvent then dissolves the exposed region of the film, leaving a nanostructured polymer behind. Later this nanostructure is transferred into the silicon through a reactive ion etch. While the nanostructured polymer is transferred, the surrounding material properties are of paramount importance to the quality of the final structure. There are capillary forces from the aqueous solvent that can deform or collapse neighboring structures if the dimensions are small enough. To avoid this, polymers need materials properties such as the elastic modulus and it crucial if reduced dimensions affect the modulus of the nanostructured polymer. In this work we use Brillouin scattering to quantify the acoustic modes in polymer thin films and nanostructured parallel lines. In the films we see the traditional surface (Rayleigh) and longitudinal guided modes, and these can be used to estimate the bulk and shear modulus of the polymer film. In the nanostructured parallel lines, we observe an additional mode that appears to be a breathing mode of the line. We study this breathing mode as a function of line thickness in both the lithographically prepared polymeric structures as well as corresponding structures once they transferred into the silicon oxide substrate via a reactive ion etch. The possibility of using these modes to extract reliable mechanical properties is discussed in detail.

2:30 PM U5.4
NANOINDENTATION OF POLYMER FILMS TO ESTABLISH CONNECTIONS BETWEEN NANOSCALE STRUCTURE AND MECHANICAL PROPERTIES.
Matthew R. Begley and Kyle C. Muser, University of Virginia, Charlottesville, VA.

We report a thorough nanoindentation study of glassy polymer thin films, both homogeneous and micro-phase separated at the 50nm scale. Growing evidence suggests that the thermomechanical properties of polymer materials depend on the experimental length scale at small dimensions. For instance, the elastic modulus of thin
polymer films has been shown to depend on film thickness. Recent results from our group have indicated an intimate link between the density of macromolecular segments and differences in the plastic relaxation events in glassy polymers. Thus, marked changes in the plastic properties must be expected as the experimental length scale approaches the mean distance between entanglements. Our study therefore focuses on the PS/PPO compatible blend system, in which $\eta_c$ can be controlled by composition. Thin films of different composition with thickness on the order of 1000 nm were created via spin-casting, and tested via nanoindentation in a variety of tests depending on the deformation method. An improved load-to-indentation of asymmetric freestanding membranes has been developed, using a combination of spin-coating and preferential etching of the matrix materials. The additional tests are designed to identify substrate effects on both material properties and test interpretation. These tests and accompanying numerical models will be discussed in the context of (i) clearly identifying scale dependence of mechanical properties from direct nanomechanical characterization, and (ii) test scale characterization of the intrinsic deformation in polymers. In extension of the above work, results will also be presented on polyethylene-ethylene-propylene diblock copolymers, which were observed on a length scale of about 50nm, and on a novel class of block copolymers based on metataxial diblock linkages.

**2:45 PM U5.5**

**EFFECT OF TEMPLATING BYPRODUCTS ON ADHESION OF NANOPOROUS THIN FILMS.** Dan A. Maidenhead, Stanford Univ., Dept of Materials Science and Engineering, Stanford, CA; Willi Volksen and Robert D. Miller, IBM-Almaden Research Center, San Jose, CA; Reinhard Kratky, Stanford Univ., Dept of Materials Science and Engineering, Stanford, CA.

From biological scaffolds to dielectric layers in microelectronics, nano-templated organo-inorganic hybrid materials are being developed to provide a versatile class of highly porous materials with tunable properties. Through selection of porogen molecules, controlled nanometer-sized pores may be produced at selected volume fraction. However, while materials may be designed for electrical, optical, or even biological properties, the incorporation of porosity may significantly affect the mechanical properties of the material, especially as they relate to fracture toughness and adhesion to adjacent materials. Generally, the fracture toughness of brittle glasses is known to degrade in the presence of porosity, and such behavior has also been found for thin porous films. In the present study, we demonstrate that with appropriate selection of MSSQ precursors and porogen molecules, highly porous films may be created that exhibit remarkable adhesive and fracture resistance properties. Treatments of the porous layer involving exposure to UV/ozone was found to increase the adhesive properties of films containing 50% porosity by an order of magnitude, from 2.3 $\mathrm{mJ/m^2}$ to over 20 $\mathrm{J/m^2}$. Such unique effects on mechanical behavior are described in terms of molecular byproducts of the pore creating process itself, specifically pore-wall residues that create specific bridging mechanisms to improve fracture resistance. Detailed characterization results together with modeling of the toughened mechanisms are discussed.

**3:30 PM U5.6**

**GREEN NANOCOMPOSITES – PATHWAY TO THE FUTURE FOR HIBASED POLYMERS.** A.K. Mohanta, L.T. Drzal and M. Misra, Composite Materials and Structures Center, Department of Chemical Engineering and Materials Science, Michigan State Univ. East Lansing, MI.

Environmentally benign materials (EBM) are the wave of the future to save our world from growing pollution threat. Biopolymers are now moving into the mainstream and the polymers that are biodegradable or based on renewable “feedstock” may soon be competing with the commodity plastics. Performance limitations and high cost have put these biopolymers aside and makes them unattractive. However, in the last years, green plastics including cellulose esters [plastics made from wood cellulose], polylactides or PLA (corn-derived plastic) and polylactides/amides (bacterial biopolymers) have attracted recent attention in potential replacements of existing fully petroleum-based non-biodegradable polymers both on cost and performance basis with added advantages of bio-originated and eco-friendliness. To find new and emerging applications of biopolymers through innovative technology is a formidable task for scientists. The nanoreinforcement pose a bright future for biopolymers in finding new green nanocomposite materials for various applications in green automotive parts, electronic cases and green packaging. Green nanocomposites are fabricated from biopolymers and organically modified clays through melt-processing route. Effects of process engineering on performance of nanocomposites are analyzed. We found that extrusion followed by injection molding rather than extrusion followed by compression molding exhibits an improved performance of biopolymer/green nanocomposites. Through TEM studies, the differences in nanocomposite performances of such two processing approaches are explained. Extent of intercalation and or exfoliation of nanofillers in polymer matrix are responsible for improved mechanical properties of the nanocomposites. True nanocomposites exhibit improved strength/stiffness without sacrifice of toughness besides showing much reduced gas permeability (improved barrier properties), lower coefficient of thermal expansion (CTE), improved heat deflection temperature and reduced water absorption. This presentation will give an overview on the current status and future prospective of biodegradable polymer - clay based green nanocomposites and will highlight the importance of research involved in this area for the performance of the emerging green plastics. Acknowledgements: This research is supported by NSF-NER 2002 Award No. BES-0210881.

**3:45 PM U5.7**

**HIGH STRAIN-TO-BREAK VALUES OBSERVED IN PERIODIC SILICA/POLYMER COMPOSITE MATERIALS.** Bradley L. Kirsch, Sarah H. Tolbert, University of California, Los Angeles, Dept. of Chemistry and Biochemistry, CA; Jin Tian, Vijay Gupta, University of California, Los Angeles, Dept. of Mechanical & Aerospace Engineering, Los Angeles, CA.

Disordered inorganic/organic composites are lightweight materials that potentially hold promise for a variety of applications, but generally have poor mechanical stability. However, it is possible to produce well-ordered inorganic/organic composites that exhibit long-range periodicity using self-assembly techniques. Recent results demonstrate that these periodic composites exhibit superior compressive properties compared to disordered systems. In this work we explore how ordering inorganic/organic materials affects the tensile properties of highly-ordered Si/silica/polymer composite films. We show that the absolute value of the tensile strain to break is larger than that of bulk silicon. We also show significant differences in the strain-to-break values between the films parallel and perpendicular to the cylindrical organic domains. These results are strong indications that the mesoscale hexagonal architecture produces the superior mechanical properties. The ratio of the strain to break in the parallel direction to the strain to break in the perpendicular direction is approximately constant with variable film thickness, while the magnitude of the strain to break in both directions is proportional to the film thickness. This demonstrates that the phenomenon is not simply a thin film effect, but rather a property that is inherent to the well-ordered mesostructure. We have also modeled this system using finite element analysis, and the results are in good agreement with the experiments. This work demonstrates the utility of tailoring properties on different length scales to produce desirable mechanical properties in nanoscale materials.

**4:00 PM U5.8**

**SYNTHESIS AND PROCESSING OF SINGLE-WALL CARBON NANOTUBES/CEMATIC NANOCOMPOSITES WITH NOVEL PROPERTIES.** Gwo-Dong Zhan, Joshua D. Kuntz, and Aminy K. Mukherjee, Department of Chemical Engineering and Materials Science, University of California - Davis.

The extraordinary mechanical, thermal and electrical properties of single-wall carbon nanotubes (SWCN) have prompted intense research into a wide range of applications in materials, electronics, chemical processing, and energy management. There have been many predictions of the reinforcing effects of carbon nanotubes in various composite matrices but large improvements in properties have not yet been convincingly demonstrated. For instance, only a slight increase in toughness has been obtained in aluminum based systems. In the present study, we have successfully realized this possibility in reinforcing nanocrystalline ceramic nanocomposites for the first time. Fully dense SWCN/alumina nanocomposites with nanocrystalline alumina matrix have been fabricated at sintering temperatures as low as 1423 K by novel spark-plasma-sintering. A great improvement in fracture toughness has been achieved in these nanocomposites. Microstructural investigations have revealed that the effective bonding of ropes with the matrix plays a central role in the reinforcing effect. This investigation was supported by a grant (SF-G05541-00-L1085) from US Army Research Office with Dr. William Mollies as the Program Manager.

**4:15 PM U5.9**

**PARAMETRIC RESONANCE BEHAVIOR AND MECHANICAL PROPERTIES STUDIES IN NANO-FIBERS.** Mei-Ling Min-Feng Yu, Univ. of Illinois at Urbana-Champaign, Dept. of Mechanical and Industrial Engineering.

The extremely small dimensions of nanomaterials imply unique mechanical/electronic properties for their potential applications, which, however, also impose great challenges for many experimental studies. We developed a nanomanipulation device for use inside a scanning electron microscope, which is capable of nanoscale resolution motion, and free-space manipulation and characterization.
of nanostructures. We report the realization of parametric resonances of individual nanowires using an oscillating electric field. Resonances as driven the 300 GHz, where the nanowire's fundamental resonance, for n from 1 to 4, were observed and analyzed. (High order parametric mechanical response for n up to 4 was only recently observed in microwind MEMS resonators.) Regions of instability were mapped, and hysteresis in the parametric response was observed. A theory that includes a forcing term proportional to the amplitude of the response was used for the analysis, which agrees well with the experiment. The resonances were found to originate from the incident electric field exciting the nanowire, and can be described by the Mathieu equation, which has known regions of instability in parametric space. We will also report the studies of other mechanical properties (modulus, tensile and shear strength, and deformability) of various nanostructures (nanotube, nanowire and nanoribbon) using the free-space manipulation and characterization technique, and advanced microscopy. See references: Min-Feng Yu, et al. Phys. Rev. B 64, 241406R (2001); Min-Feng Yu, et al. Phys. Rev. Lett. 85, 1456(2000); Min-Feng Yu, et al. J. Phys. Chem. B. 104, 8264(2000); Min-Feng Yu, et al. Phys. Rev. Lett. 84, 5552(2000); Min-Feng Yu, et al. Science 287, 467(2000).

4:30 PM US.10
NANO-MECHANICAL IMAGING OF MULTI-WALLED CARBON NANO TUBES. Laxma Mathur, University of Science, University at Albany, Albany, NY; P. M. Ajayan, Dept of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY; Robert Geer, School of NanoSciences, University at Albany, Albany, NY.

Carbon nanotubes represent a singular example of a molecular system offering emergent functionalities derived from its nanoscale size. It has been aggressively researched for uses in nanocomposites owing to its outstanding mechanical properties (both its metallic and semiconducting character). To date, experimental investigations of the mechanical properties of individual nanotubes have treated the entire tube as a classical uniform beam or cylindrical shell and derived elastic information (modulus, Poisson's ratio, etc.) based on those assumptions. To investigate intra-tube variations of mechanical response the nanomechanical mapping of individual multi-walled carbon nanotubes (MWNs) has been undertaken. Ultrasonic resonance mapping has been used to measure the radial and axial variations of contact stiffness of individual MWN's synthesized using chemical vapor deposition (CVD) and arc-discharge (A-D) techniques. For CVD-based MWNs the contact stiffness of the tube was seen to vary strongly across volume defects (axial variation of the tube radius) and is assumed to result from the high crystaline defect density associated with such radial variations. These observations support recent experimental data of effective Young's modulus inferred from nanotube vibration amplitudes. Discrete mechanical defects have also been imaged in A-D MWNs for which the radius is constant as a function of axial position. Local continuum elastic models are used to quantify the contact stiffness over small (10 nm x 11 nm) regions of the tube.

4:45 PM US.11
SIMULATION OF LOW-STRUCTURED COLLOIDAL SILICA NANO PARTICLES FOR REINFORCEMENT IN SILICONE ELASTOMERS. Timothy C. Chao, Dow Corning Corporation, New Ventures R&D, Midland, MI; Deborah F. Bergstrom, Dendritic Nanotechnologies Limited, Mount Pleasant, MI.

Aqueous suspensions of colloidal silica are readily synthesized with chlorosilanes in the presence of acid and isopropyl alcohol without aggregation of the silica particle. By using a mixture of chlorosilanes, spherical nanoparticles with controlled functionality can be made and transferred to an organic phase to provide stable, water free suspensions. The hydrophobic colloidal silica particles readily disperse into silicone polymers. In order to provide mechanical reinforcement comparable to traditional fumed silica, high filler loading of about 30 wt. % was used. The unique low-structured pearl necked-shaped colloidal silica become commercially available. These nanoparticles are successfully sylized and they maintain the original structure as evidenced by transmission electron microscopy (TEM). They are compounds into silicone polymers at 25 - 30 wt. % and they provide excellent viscosities and mechanical properties, especially the tear strengths. In this presentation, the synthesis, characterization and mechanical properties of colloidal silica nanoparticles in silicone elastomers will be covered.

SESSION US.6 POSTER SESSION

Chairs: K. Paul, D. Hall and H. King
Wednesday Evening, April 23, 2003
8:00 PM - 9:30 PM
Golden Gate (Marriott)

U6.1 ANALYSIS OF DISLOCATION NUCLEATION UNDER A NANOINDENTER. Chunhui Zhang, Gaohuang Xu, Department of Mechanical Engineering, University of California, Riverside, CA.

We present an analysis of dislocation nucleation under a nanoindenter based on the Peierls-Nabarro dislocation model. By incorporating atomic information into the variational boundary integral method, we have determined the embryonic dislocation profiles and the associated activation energy required to activate the dislocations from the immobile to unstable state. Depending on the loading conditions, we also obtained the indentation force and displacement relation for a case that involves nucleation of multiple discrete dislocations under the indenter. The results have direct correlation with the recently observed discrete plastic deformation in nanoindentation experiments.

U6.2 DEFORMATION PROCESSES DURING NANOINDENTATION OF Ti3SiC2, A. Murugan, M.W. Barsom, S. Kalidindi and T. Zhao, Department of Materials Engineering, Drexel University, Philadelphia, PA.

This paper discusses the deformation processes during the nanoindentation of Ti3SiC2, a thermodynamically stable nano-luminate. In this presentation we report on the load-depth-of-indentation response of Ti3SiC2 surfaces loaded with a 13.5 μm spherical tipped diamond indenter up to loads of 500 mN. Combining scanning electron microscopy and orientation imaging, two surfaces were identified; one in which the basal planes were parallel to, and the other normal to the surface. Not surprisingly for such a plastic-anisotropic material, the response was anisotropic and comprised of two regimes. At the higher loads (200-500 mN) damage was initiated and resulted in delaminations when loaded parallel to, and smaller microcracks when loaded normal to the basal planes. At lower loads (50 mN), the response was unique to Ti3SiC2 and resulted in almost fully reversible closed hysteresis loops. Subsequent repeated (up to 5) loadings on the identical location only did result in fully reversible, reproducible hysteresis loops, but resulted in the hardening of the indented volume. Despite the fact that the hardness stresses at the tip of the indenter were of the order of 15 GPa and the repeat nature of the loadings, almost no trace of the indentations were found. This response is believed to be due to the formation of microcrack incipient and regular kink bands. In this respect it is not unreasonable to think of Ti3SiC2 behaving as a dislocation-based elastomer in the sense that it can be loaded repeatedly without damage and dissipate significant amounts of energy during each cycle.

U6.3 DEFORMATION OF SMALL VOLUMES OF MATERIAL STUDIED USING STRAINED LAYER SUPERLATTICE STRUCTURES. K.M. Pong, A.J. Bashby and D.J. Dunstan, Centre for Material Research, Queen Mary, University of London, UNITED KINGDOM.

Mechanical studies of semiconductor superlattices have shown that the onset of plastic deformation under an inhomogeneous stress is a process that takes place simultaneously across a finite volume of the order of a micron across. The deformation behaviour of materials under contact loading is of prime technological importance and the criterion for yielding is important as a design tool. As technology moves increasingly to smaller scales in thin film coatings, nanostructured materials and micro-electro-mechanical systems, existing yield criteria fail rather badly. The ability to incorporate known internal stresses, and to vary the stress and thickness of individual layers in a semiconductor superlattice, is a very powerful tool, opening up new possibilities for investigations that cannot be achieved by varying external stresses on a specimen that is sensibly homogeneous. In this way, from the initial yield stress of single-crystal strained-layer superlattices under indentation, we demonstrate a new criterion, of which the key feature is that it is to be averaged over a finite volume. By careful nanoslicing of individual layers and in bands forming low yield stress material within the structure, the size and position of the initial yield can be determined and the yield criteria deduced.

U6.4 NANOINDENTATION TESTING TO OBSERVE SLIP TRANSFER ACROSS GRAIN BOUNDARIES. K.A. Niran, D.P. Bahr, and D.P. Field, Washington State University, Configural and Materials Engineering, Pullman, WA.

Nano crystalline materials are increasingly coming into the focus of cutting edge metalurgy. With it comes the importance of understanding and predicting how dislocations are able to transfer across grain boundaries. Current empirical techniques for observing slip across boundaries relies heavily on the use of TEM which is effective, but also technically challenging and time consuming. Recent advances in indentation testing coupled with orientation imaging...
microscopy allow slip across grain boundaries to be easily observed and measured. Because of the relative ease of this procedure, numerous boundaries of different misorientation in a reasonable time span. Atomic force microscopy reveals slip steps on the surface around an indentation. These steps can be used to determine the active slip system. When slip crosses a boundary, the steps visible in each grain identify all active slip systems that intersect the free surface. The extent of slip transfer can be compared with different strain fields as well as variations in the angle between intersecting slip planes within the boundary. A series of nonindented grains along grain boundaries of various misorientation angles in large grained materials is presented to demonstrate this technique. Comparisons are made with indentations in fine grained materials to understand nonindentation results from monoclinic alkali salts.

U6.5 INTERFACIAL STUDIES IN CLAY POLYMER NANO. COMPOSITES. H.A. Goldberg, C.A. Feney, M. Farell, D.P. Krimm, Inc/LLC; G. Collins, Z. Ophir, and M. Jaffe, Biomedical Engineering, NJIT.

Clay polymer nanocomposites have been shown to provide large improvements in both the barrier properties and modulus over unfilled polymers. On the other hand, in most cases, the strain to failure is significantly reduced. In order to control the flexibility of these materials it is important to also control the degree of dispersion and the interactions between the nanodispersed clay and the polymer.

In Mrs. elastomeric barrier coatings provide an example of a nanocomposite system in which the filler dispersion can be controlled, and the degree of flexibility provides evidence for good dispersion. Typically, a mineral filler in an elastomeric matrix would lead to a large reduction in flexibility. However, In Mrs has shown that control over the inner interface can produce this loss in flexibility. More direct evidence for particle dispersion has proved hard to acquire. For example, electron microscopy is difficult due to the elastomeric matrix. In this paper, we will discuss the use of thermally stimulated current measurements (TSC) as a tool that is sensitive to the clay-polymer interface. We will discuss its utility in determining the mobility of polar species at the interface. We will compare these results with DSC, thermal expansion, and mechanical measurements in order to determine the utility of this technique for understanding clay polymer nanocomposites. Special attention will be paid to the choice of matrix and exfoliated clay and their role in determining the composite properties.

U6.6 DUAL TRIBOBIOLOGICAL BEHAVIOR OF A NANO LAYERED CERAMIC: Ti3SiC2. Alexandre Schaudy, Julien Fontaine, Michel Belin, Thierry Le Maguer, Jean-Luc Lelubre, Ecole Centrale de Lyon, Laboratoire de Tribologie et Dynamique des Systèmes, Écully, FRANCE; Michel W. Barsoum, Drexel University, Department of Materials Engineering, Philadelphia, PA.

The MAX phases are new, thermodynamically stable, nanolayered ternary carbides and nitrides. These materials can have a high potential in tribological applications due to their structure, as graphite or molybdenum disulfide. For example, the band gap of Ti3SiC2 is 6 eV and the electrical conductivity is 1000 times larger than that of stainless steel. MAX phases have been used in a variety of applications, such as tribological coatings. However, the low friction coefficients and electrical contact resistance. Differences in the properties of different materials and their use in contact conditions have been shown to affect contact pressure. In this work, we report on the behavior of a MAX phase, Ti3SiC2, in contact with stainless steel. Two different tribological behaviors were observed, both with relatively low friction coefficients.

The first behavior, referred to as type I, is characterized by a friction coefficient of 0.15. Wear of Ti3SiC2 plane is low and a transfer film of titanium and carbon is formed on the ball. The second behavior, type II, is characterized by a friction coefficient that starts at 0.15 and increases to 0.4. The effect of the experiment, the ball is worn, and compacted wear debris containing iron can be found on the plane. The two behaviors seem to be independent of contact pressure, but are rather sensitive to normal applied load. The transition between these two regimes will be discussed, in light of electrical contact measurements during sliding.

U6.7 MECHANICAL PROPERTIES OF NANO STRUCTURIZED AND PREVIOUSLY CASTED POLYMERS GROWN BY PULSED LASER DEPOSITION. Hyunbin Kim, Shane A. Cate,jode, Yogesh K. Vohra, and Renzo P. Cammar, University of Alabama at Birmingham, Dept. of Physics, Birmingham, AL; William R. Lacefield, University of Alabama at Birmingham, Dept. of Prosthodontics and Biomiaterials, Birmingham, AL.

Hydroxyapatite (HA) [Ca10(PO4)6(OH)2] among calcium phosphates is commonly coated onto orthopedic and dental metallic implants to improve the bone formation, devices, allowing enhanced bone implantation in a patient. Studies in the past decade have indicated that pulsed laser deposition (PLD) may be the most suitable means of placing thin HA coatings on these implants because of its demonstrated control over stoichiometry, microstructure, and nanostructure. These characteristics determine the mechanical properties of the films that must be optimized to improve the performance of load-bearing implants and other devices that undergo bone insertion. In this work we used PLD to produce nanostructured polycrystalline HA coatings and evaluated their mechanical properties. Pure, highly crystalline HA coatings on Ti-6Al-4V substrates were obtained using a Q-switched "Er:Cr:YSGG" excited laser (266nm) with energy density of 4-8J/cm2 and deposition temperature in the range of 500°C~700°C. Scanning electron and atomic force microscopy reveal that our careful manipulation of energy density and substrate temperature has led to films made up of HA grains in the nanometer scale. Broadening of x-ray diffraction peaks as a function of deposition energy density suggests that it may be possible to control the film microstructure to a great extent. X-ray diffraction also show that as the laser energy density is increased in the 4-8J/cm2 range, the coatings become preferentially oriented along the c-axis perpendicular to the substrate. Nonindentation measurements show improved hardness and Young's modulus in oriented films that can be attributed to the crystalline alignment in the nanotwinned hexagonal HA structure caused by the high energetic plasma during deposition. Preferential orientation, nanostructure, and phase make-up all significantly influence the mechanical properties. We will discuss how each of these factors affect hardness and Young's modulus of the HA films. (Funded by NIH: NIDCR R01 DE035952-02-A1, NSF: DMR-0116988).

U6.8 MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NANO LAYERED TiN/Cu THIN FILMS. You You Tae, Abad Al-Adami, Gregery, Ann Michel, Christophe Tounouch, Michel Jansen, Laboratoire de Métallurgie Physique, Université de Poitiers, Futuroscope-Chasseneuil, FRANCE.

Metal/Nitride composite thin films, either in the form of biphase monocomposites or multilayers, have attracted considerable interest for their improved mechanical properties. The present study is focused on the TiN/Cu system, of which a strong mechanical (huge difference in shear modulus) and structural (large misfit of 15%) contrast exists between the two materials, making it a promising system to study the interplay between the growth mode, resulting microstructure and mechanical behavior. TiN/Cu multilayers were grown by high vacuum dual ion beam sputtering deposition with bilayer period ranging from 3 to 50 nm. Both low-angle and high-angle X-ray diffraction (XRD) experiments have been employed to globally characterize the multilayers structure. High angle XRD spectra revealed a [002] TiN and [002] Cu texture, while pure Cu films on Si (001) exhibited a strong [111] texture. Analysis of the stress/strain at the TiN/Cu multilayers by the "w" method, and the TiN layers are under large compressive stress, while the Cu layers are under small tensile stress. The microstructure of the multilayers has been characterized using HRTEMs. A cube-on-cube epitaxial growth mode of Cu on TiN was identified, the presence of [111] faceted islands as well as several lattice defects have been observed in the Cu layers. The effects of interface and bilayer thickness on hardness were investigated by reflection-sensitive X-ray diffraction technique. A small hardness increase with decreasing periodicity of the structure is observed. The relationship between the h/T ratio and the hardness, where h, is the contact depth and T the total film thickness, was established. The effects of substrate on film hardness were studied by comparison between films deposited on MgO [001] and Si [001] substrates, respectively. The composite hardness on MgO substrate renders larger hardness values than those on Si substrate by about 20%. The effect of pop-in phenomenon in MgO on the resulting hardness for h/T>0.2 will be studied. The relationship between the microstructure and hardness were discussed in terms of mechanical models.

U6.9 POINTWISE SYNCHROTRON STRAIN MAPPING OF RELEASED MEMS GOLDILOK. V.N. Pedro, S. S. Vlahos, University of Michigan, Dept. of Electrical Engineering, Ann Arbor, Michigan, USA; R. Clarke, University of Michigan, Dept of Physics and MIATT-CAT, Ann Arbor, MI; D.A. Walko, Argonne National Lab, Advanced Photon Source, Argonne, Il; D.J. Dagel, D.P. Adams, Sandia National Labs, Albuquerque, NM.

We have used a micron-sized x-ray beam at the Advanced Photon Source to measure and profile strain across a prereleased, 250 micron diameter silicon cantilever microsensor. A 100 μm wide x-ray beam was focused using two bendable Kirkpatrick-Baez mirrors to a ~40 μm spot size and used to measure strain at various points across
the micromirror surface. The 2.25 micron thick polysilicon mirror was coated with a low stress, high reflectivity multilayer film of 350nm Ti/100nm Au by sputtering. Provisions for Au and Si planes were measured to assess in-plane and out-of-plane strain, which were then related to the micromirror curvature.

**U6.10 TEXTURE AND NANO HARDNESS OF YSZ ELECTROLYTE THIN FILMS PREPARED BY COMBUSTION CVD AND PULSED LASER DEPOSITION**
Zhenguo Xu, Sergey Yarmolenko, Qag Sankar, NSF Center for Advanced Microsystems for Smart Structures, North Carolina A&T State University, Greensboro, NC.

Yttria-stabilized cubic phase zirconia (YSZ) has been used as an electrolyte in solid oxide fuel cells (SOFCs) and oxygen sensors because of its high oxygen ion conductivity over wide range of temperature and oxygen pressure. Thin film is preferred for the YSZ electrolyte in order to minimize the current path in the fuel cell. Present research is geared towards the improvement of fuel cells efficiencies through understanding various materials issues and their performance against the environmental conditions. In this paper, fundamental understanding of hardness and modulus of the film and knowledge concerning the influences of the substrate/interface and crystal sizes on the overall behavior of the electrolyte thin film will be presented. The YSZ thin films were synthesized with atmospheric combustion chemical vapor deposition (ACCVD) with liquid fuel and pulsed laser deposition (PLD) techniques on Si(100) and MgO(100) substrates. The particle sizes were controlled in the range from submicron to several nanometers. To increase the strength and ion conductivity of the YSZ thin films, composite films of YSZ and Al2O3 (<10 mol %) were processed. The as-grown films were characterized with X-ray diffraction, scanning electronic microscopy and transmission electron microscopy to identify their microstructures. The effect of the particle size and the addition of Al2O3 on the mechanical properties of the films was determined by nanoindentation techniques. The relationship between micro- mechanical properties, microstructures, and the processing parameters were optimized for desired mechanical properties.

**U6.11 USING FLUCTUATIONS TO LOCATE THE SURFACE ROUGHENING TRANSITION**
David Bentley, Kenneth Judson, University of Arizona, Dept. of Materials Science and Engineering, Tucson, AZ.

We have conducted a kinetic Monte Carlo study of the surface roughening transition of the [100] FCC surface by using fluctuation dissipation theory to determine the kinetic coefficients. The simulations were conducted using a spin 1/2 Ising model treatment of the solid-liquid interface with simulation cells 50 by 50 by 10 lattice units in size. Interfaces were studied at equilibrium with an imposed temperature gradient to supply a restoring force for the interface. Fluctuations in the number of solid atoms in the system about the equilibrium positions were examined using time correlation functions. These characteristic times were used to calculate the kinetic coefficients of the system. We have observed a dramatic change in these characteristic times which locates the surface roughening transition.

**U6.12 ATOMIC MODELLING OF THE DEFORMATION BEHAVIORS OF NANO MATERIALS**
K. Sreekanta, T. Nakajima, Y. Nakura, and S. Kumecke, Dept. of ME & Intelligent Sys., Kyushu University, Tokyo, Japan.

Nanomaterials such as carbon nanotubes, semiconductor nanowires, metallic nanowires, and nanowinders have a wide variety of applications in the fields of nanotechnology. Carbon nanotubes are about to emerge in the market as a material for electrodes of field emission displays. They are also promising as materials for probe tips of scanning probe microscopes and nanosensors or nanoelectronics. Rapid progress of the growth methods of semiconductors has realized nanowire junctions and nanowire superlattices which will open the world of nanodevices. Metallic nanowires have drawn much intention of researchers since the linear strain of gold atoms at a nanomesh between a scanning tunneling microscopic probe and a metal surface was observed. These nanowires are probably applicable to wiring in nanocircuits. Both knowledge of the mechanical properties of nanomaterials and understanding of their deformation mechanisms are essential to realization of all of these applications. In the application of carbon nanotubes to nanoelectronics which hold nano-structured strength and large deformation characteristics should be known beforehand. In this study, some atomic models for the deformations to nanomaterials are proposed, and molecular-dynamics simulations based on such models are performed for elongation, compression, bending, and torsion.

**U6.13 CORRELATION BETWEEN MECHANICAL AND STRUCTURAL PROPERTIES OF TiC AND TiCN THIN FILMS GROWN BY RF SPUTTERING**
Abderahman Mansi, Pascal Aubert, Philippe Houdry, Université Evry Val Essonne, Laboratoire Géométrie Nanostructure (LabM), France; Hechan Khodja, CEA/DSM Laboratoire Pierre Gif-sur-Yvette, FRANCE; Florence Mercier, Université Evry Val Essonne, Laboratoire Analyse et environnement, FRANCE.

Titanium carbide, TiC, and titanium carbonitride, TiCN, thin films present attractive mechanical and tribological properties for engineering applications. The aim of this study is to correlate the mechanical properties of TiC and TiCN thin films with the structural properties and chemical composition analysed by X-Ray Diffraction, Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis. Mechanical properties were determined by nanoindentation and were correlated to intrinsic stress calculated by Stoney formula. Thin films of TiC and TiCN were deposited on c (100) silicon substrate by RF sputtering from a Ti-C target using respectively an Ar plasma and an Ar-N2 plasma. Various sputtering total pressure from to 0.35 to 1 Pa and sputtering power from 100W to 300W were used. For TiCN samples various Ar/N2 ratio were used. Apparently linear correlation between intrinsic stress and hardness were found for TiC films. However the hardness increase when the sputtering pressure decrease. The maximum of the hardness, 28 GPa, was obtained for thin films deposited at 0.35 Pa which present a dense structure and a high intrinsic compressive stress of 4.4 GPa. Thin films TiCN were produced at total pressure equal to 0.35Pa with various N2 partial pressures ranging from 1% to 50% of total pressure. A hardness of 20GPa was achieved and related to the chemical composition. Finally first results of TiC/TiCN multilayers will be presented.

**U6.14 MECHANICAL PROPERTIES OF NONSTRUCTURED METAL-CERAMIC THIN FILMS**
D. Kumar, N. Sudhir, S. Yarmolenko, and J. Sankar, Center for Advanced Materials and Smart Structures, Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Thin films composite materials consisting of metallic nano-crystals embedded in an insulator host have been synthesized using alternating target pulsed laser deposition of Fe/Ni and Al2O3. The evaluation of structural quality of the thin film composites using high resolution transmission electron microscopy and scanning transmission electron microscopy with atomic number contrast has revealed the formation of a high-sheared system with thermodynamically driven segregation of Ni and alumina during pulsed laser deposition. The best hardness values of the thin film composites, measured using nanoindentation techniques, was found to be 29.05 GPa, which is larger than pure alumina films fabricated under identical conditions. The improvement in hardness of Al2O3 thin films by embedding metal nano-crystals is related to the microstructure of a material, which efficiently hinders the manipulation and movement of dislocation and the growth of microcracks, which in turn, is achieved by grain boundary hardening.

**U6.15 DETERMINATION OF Ag/NI INTERFACIAL FREE ENERGIES BY BIAxial zero CReep Experiments**
Ding An, Tong-Jie Zhang, Min Shao, Guanghua University, Technical Key Laboratory of Die and Mould Technology, Wuhan, P.R. CHINA; Wei Zhang, University of Maryland, Gaithersburg, MD.

Biaxial zero creep experiments were performed on Ag/ni multilayer films on Si (111) substrates. An optical apparatus with parallel multi-beams and CCD detector was used for monitoring the curvature changes during heating process. The equilibrium curvature was measured to determine the interfacial free energy of Ag/ni interfaces, and thereafter their effects on the structural stability of multilayers were investigated. The residual stresses in the Ag/ni multilayers were slowly built up to zero when heating to room temperature from room temperature to 450°C. The equilibrium curvature was reached soon after hitting 450°C, and after a long time at this elevated temperature, it seems that no change occurred. Based on the equilibrium between interfacial residual stress and interfacial free energy, a free energy of Ag/ni interfaces at an equilibrium temperature of 450°C could be determined.

**SESSION U7 FAILURE AND FRACTURE IN NANO MATERIALS**
Chairs: Neville R. Moody and Anna C. Balazs Thursday Morning, April 24, 2003 Metropolitan I (Argent)**
8:30 AM • U7.1
THE INFLUENCE OF GRAIN SIZE ON THE FATIGUE BEHAVIOR OF OTHER CRYSTALLINE FILMS. Oliver Kräf, Cynthis A. Vokkert, Forschungszentrum Karlsruhe, Institut für Materialforschung II, Karlsruhe, GERMANY; Ruth Schwenk, MPI, Dept. of Material Science & Eng. Cambridge, MA; Patrick Waller, Renier Meiring, Ongamagntra Zhang, Christoph Eberl, Ralph Spolenak, Eduard Arzt, Max-Plank-Institut für Metallforschung, Stuttgart, GERMANY.

Nanocrystalline metallic materials are known to have a very high strength compared to their large grain counterparts. However, very little is known about the fatigue behavior of nanocrystalline materials. It is the aim of this paper to discuss the change in fatigue behavior of thin polycrystalline metal films as a function of film thickness and grain size in the range from a few microns to 50 nm. Cu, Ag and Al films on substrates were subjected to cyclic deformation, which was induced either by mechanical, thermomechanical or deformational loading. Resulting frequencies ranged from 0.1 to 10 Hz. The fatigue damage was found to depend strongly on film thickness and grain size, and to be quite different compared to bulk materials: Failure of thinner films with grains larger than approximately 0.5 μm is associated with the formation of extrusions at the surface and voids near the film/substrate interface in the interior of the grains. Transgranular cracks are generated from these voids at the film substrate/interface rather than from the film surface. However, in thinner films with fine grains, damage exhibits an intergranular growing, voiding and possibly cracking while extrusions are still present at the film surface. Furthermore, transmission electron microscopy investigations show a general trend of precipitation density in fatigued film increases with decreasing thickness and grain size. These findings indicate that fatigue in nanostructured metallic materials appears to be controlled by dislocation mechanisms and interface properties rather than by dislocation glide and bulk properties.

9:00 AM • U7.2
FATIGUE DEGRADATION OF NANO-TUBE-SCALE SILICON DIOXIDE/REACTION LAYERS ON SILICON STRUCTURAL FILMS. Christopher L. Middle, The Pennsylvania State University, Dept. of Materials Science and Engineering, University Park, PA; Eric A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; William C. Jones, National Nanotechnology Coordinating Division, Logistics Berkeley National Laboratory and Dept. of Materials Science and Engineering, University of California, Berkeley, CA.

Although bulk silicon is ostensibly immune to cyclic fatigue and environmentally assisted cracking, the thin film form of the material exhibits significantly different behavior. Such silicon thin films are used in small scale structural applications, including microelectromechanical systems (MEMS), and display "metal-like" stress-life / S / N fatigue behavior in room temperature air environments. Fatigue lives in excess of 10^11 cycles have been observed at high level (σ / d / t) fully-reversed stress amplitudes as low as half the fracture strength using surface micromachined, resonant-loaded, fatigue characterization structures. Recent experiments have clarified the origin of the susceptibility of thin film silicon to fatigue. Studies utilizing electron microscopy, infrared microscopy, and numerical modeling techniques were used to establish that the mechanism of the apparent fatigue failure of thin-film silicon involves sequential oxidation and environmentally assisted crack growth solely within the nanometer-scale silicon layer on the surface of the silicon, via a process that we term 'reaction-layer fatigue'. Only thin films are susceptible to such a failure mechanism because the critical crack size for catastrophic failure of the entire silicon structure can be exceeded by a crack solely within the surface oxide layer. The growth of the oxide layer and the environmentally-assisted initiation of cracks under cyclic loading conditions are discussed in detail. Furthermore, the importance of interference between the crack growth and the synergism of the oxidation and cracking processes are described. Finally, the successful mitigation of reaction-layer fatigue with nanolayer coatings is shown.

9:15 AM • U7.3
ADHESION OF POLYMER THIN-FILMS AND PATTERNED LINES. EFFECTS OF 1-D AND 2-D CONSTRAINT FROM NANO-TO MICRON-LENGTH SCALES. Christopher S. Little, Ronald H. Dauskardt, Stanford University, Department of Material Sciences and Engineering, Stanford, CA.

Emerging nanotechnologies require an understanding of the effects of multi-dimensional elastic constraint on the mechanical and interfacial properties of complex device structures. In the present study, the adhesion of interfaces in thin-film structures containing ductile polymer thin films with patterned lines was studied. The intent of the study was to demonstrate that both the film thickness (50 nm - 5 μm) and the aspect ratio of patterned lines (2 - 12) have a significant effect on the interfacial fracture energy of interfaces adjacent to ductile polymer. There is an apparent reduction in the effect of dimensional constraint in the planes of the film on local plasticity and associated interfacial fracture energies. Accordingly, the interfacial adhesion of patterned structures containing arrays of polymer/SiO2 lines with varying aspect ratios was investigated. Microscopic adhesion values were determined by measuring the critical strain energy release rate, Gc, for delamination of the patterned interface. The yield properties of the polymer films as a function of film thickness was found to be largely insensitive to layer thickness, while interfacial fracture energy displayed a marked sensitivity to thickness. In addition, decreasing the aspect ratio of the polymer lines was found to significantly increase interface fracture energy. Behavior is rationalized in terms of the effect of stress state on the local fracture mode and the extent of plastic deformation in the polymer line.

9:30 AM • U7.4
ORIENTATION AND GRAN SIZE EFFECTS ON THE ADHESION OF THIN DUCTILE FILMS. M.J. Costill, D.F. Bahr, Washington State University, Pullman, WA.

Adhesion of thin metal films is important to the microelectronics industry. It has been shown that stress affects the properties of thin films. As the thickness of a film increases the amount of plastic deformation also increases. This increase in the plastic deformation increases the measured interfacial fracture toughness due to an increase in energy dissipation in the mode II component of loading. The thickness changes as well. The grain size can be controlled by varying the process conditions used to deposit the film, and post growth processing. In sputtering the pressure or temperature of the substrate can be controlled to produce films with a fine grain structure or large grains. Electroplating produces a fine grained film and annealing the as deposited film will increase the grain size. This study examines how the grain size will impact the mechanical properties, namely adhesion, of thin ductile films on brittle substrates. The thickness of copper and tin films remained constant while the grain size was changed using controlled process conditions. The grain structure of the films was examined using OIM and AFE. The interfacial fracture toughness was determined using a tungsten carbide indenter and mechanics based models. The hardness of the films were correlated to the measured interfacial fracture toughness, and demonstrate that increased hardness correlates to an increased sensitivity to the mode II component of loading.

10:15 AM • U7.5
EFFECT OF MOISTURE AND GRADED-LAYER MECHANICAL PROPERTIES ON DEFORMATION AND INTERFACIAL ADHESION. Lorraine C. Wang, and Reinhold H. Dauskardt, Stanford University, Department of Materials Science and Engineering, Stanford, CA.

Controlling material properties over nanometer length scales is crucial for current and emerging high-density microelectronic devices. Miniaturization of devices is increasingly limited by the ability to connect to the required physical dimensions. Thin film structures must be fabricated where layer thickness and feature sizes approach micron size scales while achieving the required mechanical, thermal and electrical properties. Second phase additions such as sub-micron sized particles are often added to locally adjust the material properties of constituent layers in the complex package structure. This results in significant variation of mechanical properties over sub-micron length scales. Such manipulation of material structure and its effects on mechanical and interfacial fracture behavior is addressed using experimental and modeling studies. Underfill layers consisting of an epoxy matrix with dispersed silica beads are shown to exhibit variations of elastic and flow properties in excess of three-fold nanostructured nanolayers thicknesses are possible by the distribution of second-phase fillers, but also by the adhesion properties of the filler/matrix interface. Interfaces are susceptible to stress corrosion cracking associated with moisture which can lead to progressive debond growth at loads much lower than that required to exceed the critical interfacial fracture energies. Subcritical debonding is affected by temperature, humidity, and the bond chemistry of the interface. The effects of these variations are considered on the adhesive and subcritical debonding toughness of adhesives. Crack behavior of polyimide is not only affected by epoxy underfill and either SiO2 or Si3N4 chip passivation. Implications for other constrained complex layered structures are considered.

10:30 AM • U7.6
We describe and demonstrate a completely new approach of
harnessing nanoscale self-assembled monolayers of enhancing
adhesion for a wide range of applications. Recently we showed that 2.5-nm-thick,
self-assembled molecular layers (SAMs) are attractive candidates for
arresting interfacial diffusion in layered structures. The rationale of using
SAMs for enhancing adhesion is based on anchoring the termini of the
molecular SAMs to the overlayers and underlayers through strong, but highly
local, chemical interactions. This unique approach has the potential to
obviates interfacial mixing typically necessary for enhancing adhesion by
conventional interleavages. These features open up the possibility for
categorization of interfacial properties for future device structures comprised
of ultrathin layers and/or molecular assemblies. We illustrate the above
caveats by using examples of mercury-free (MTPMs) at
Cu/SiO2 interfaces. The third group is chosen to effect a stronger
chemical interaction with Cu, while the silicon enables the seamlessly
anchors the SAMs with SiO2 via covalent Si-Si bonds. Four-point
bond tests of Cu/MTPMs/SiO2 show that the critical load of an
X-ray photoelectron spectroscopy (XPS) measurements of the fracture
surfaces show that delamination occurs by cleavage of the C-S bond.
Leaving the -SH groups on the fractured metal side of the interface.
No. S was detected on the SiO2 fracture surface. These results clearly
confirm our vision of using functional SAMs as adhesion enhancers.
Lower delamination energies obtained from test structures with pyridine,
and amino-terminated SAMs indicate that appropriate choice
of functional group is critical to enhance adhesion. While multi-layer
formation during nanolayer assembly is deleterious to adhesion,
molecular length of the SAM constituents does not show any
observable effect on adhesion. Based on these results, we present a model to
explain the key factors that influence adhesion in
SAM-treated Cu/dielectric structures.

11:45 AM U7.8
TRIBOLOGICAL IMPROVEMENTS IN ALUMINUM USING
PLASMA SOURCE ION IMPLANTATION SYNTHESIS OF OXIDE
NANOPRECIPITATES. Martin Bohle and Bernard Terreault,
Institut de Recherche sur les Matériaux, Université de
Quebec à Trois-Rivières, Trois-Rivières, CANADA.

Improvement of the tribological properties of pure Al and AA7075
(Al-Mg-Zn-Cu-Cr), using oxygen plasma source ion implantation
(OPSII), was investigated at process temperatures from 100°C to
460°C. Results from nanoindentation, AFM nanoscratch and XPS
chemical analysis are presented. In pure Al, low temperature treatment
(< 200°C) produced an enhancement of the surface hardness
to 3X (to 3 GPa) due to the formation of Al2O3
nanoprecipitates (~10 nm). The optimization of the mechanical
capabilities in terms of the oxygen ion dose is discussed.
At higher temperature (> 400°C), the improvement is restricted to a thinner,
brittle layer, and evidence of fracture appears in the
load-displacement nanoindentation curves. In the alloy, low
temperature treatment led to a hardness enhancement of up to 3X
to 5 GPa). Although an improvement was also obtained at high
temperature, the nano-indentation and nano-scratch were quite
different, revealing the presence of MgO nanoprecipitates (~80 nm)
to the detriment of Al2O3. Preferential Mg oxidation, as a chemical
drived force, Mg segregation, induced a complete Al surface
deposition. A moderate oxygen content (~30 %) combined with
lower temperature treatment results in better surface mechanical
improvements than extreme oxygen content and lower temperature treatment
(which may also adversely affect the bulk properties).

11:00 AM U7.9
MECHANICAL PROPERTIES OF FUNCTIONALLY GRADED
NANOSTRUCTURED METAL-CERAMIC COATINGS ON
COBALT CHROME ALLOY. Shane A. Carleide and Yogesh K.
Vohra, University of Alabama at Birmingham (UAB), Dept of
Physics, Birmingham, AL; Shann Woodard and R. Venugopalan,
University of Alabama at Birmingham (UAB), Dept of Biomedical
Engineering, Birmingham, AL.

A functionally graded nanocrystallite metallic-ceramic coating on
cobalt-chrome alloys was investigated with thin film x-ray diffraction
(XRD), nanoindentation, and scratch adhesion testing. The gradual transition
from metallic to coating bonding along with a
nanocrystallite grain structure provides a unique material system
with excellent strength, toughness, and adhesion properties. XRD
analysis of the (Co/Ni) coating indicates a cubic sodium chloride
phase with a = 4.2169(2) Å. Nanoindentation measurements of the
coating result in a hardness of 27 GPa and Young’s modulus of 320
GPa. The graded metallic/ceramic nature of the coating also results in
excellent film adhesion to the substrate.

11:15 AM U7.9
STRUCTURE AND MECHANICAL PROPERTIES OF W/WN
SUPERLATTICES. L. Maille, C. Sunt, P. Aubert and P. Garnier,
Laboratoire cédére des Milieux Nanométriques, Université d’Evry
Val d’Essonne, Evry, FRANCE.

In this paper, the structure of W, WN monolithic tungsten thin films and
W/WN superlattices has been related to their mechanical properties.
Samples have been grown on silicon substrates by reactive RF sputtering
using a nitrogen rich target W+N. The superlattice is deposited with an
atmosphere composed of a mixture Ar+N2 with two different partial
gas pressure of nitrogen : 10% and 50%. The period thickness
of multilayers was decrease from 50 to 2 nm for the two runs. The
crystallographic structure and the period thicknesses are determined by
a diffractometer (X-ray diffraction, grazing X-ray diffraction and
X-ray reflectometry). The stress of the films is obtained by an
interferometer and using the Stoney’s equation. Hardness and young
modulus are measured by nanoindentation technique combined with an
atomic force microscopy. We relate the period thickness and the
stress with the hardness of the films. The hardness of the superlattices
is increased with decreasing the layer spacing. A uniform hardness of 2.3
GPa is reached for a multilayer with a period thickness ~10 nm. This
hardness is better than W and WN monolayers prepared under the
same condition.

11:30 AM U7.10
STUDY OF THE YIELDING BEHAVIOR OF COPPER THIN FILMS ON SILICON SUBSTRATES USING MICROBEAM BENDING. L.N. Florucion, D.M. Nix, Stanford
University, Dept of Materials Science and Engineering, Stanford, CA. *Currently at Lawrence Livermore National Laboratory, Livermore, CA.

The yielding behavior of copper thin films with dimensions of 0.5 to
1.7 microns in thickness, and grain sizes in the sub-micron regime,
have been investigated using a microbeam bending method. This
method uses triangular shaped microbeams, which have the advantage
that the entire top surface of the film is subjected to a uniform state
of strain, unlike the standard rectangular geometry where bending is
concentrated at the support. With this technique, the yielding and
strain hardening behavior of Cu thin films on Si substrates has been
investigated. The Cu films were strained to fracture with a uniform pressure
up to 3X (to 3 GPa) due to the synthesis of Al2O3 nanocrystallites (~10 nm). The optimization of the mechanical
capabilities in terms of oxygen ion dose is discussed. At higher temperature (> 400°C), the improvement is restricted to a thinner, brittle layer, and evidence of fracture appears in the
type-displacement nanoindentation curves. In the alloy, low
temperature treatment led to a hardness enhancement of up to 3X
to 5 GPa). Although an improvement was also obtained at high
temperature, the nano-indentation and nano-scratch were quite
different, revealing the presence of MgO nanoprecipitates (~80 nm)
to the detriment of Al2O3. Preferential Mg oxidation, as a chemical
driven force, Mg segregation, induced a complete Al surface
deposition. A moderate oxygen content (~30 %) combined with
lower temperature treatment results in better surface mechanical
improvements than extreme oxygen content and lower temperature treatment
(which may also adversely affect the bulk properties).

11:45 AM U7.11
MECHANICAL BEHAVIOR OF ELASTOMERIC STAMPS
DURING MICROCONTACT PRINTING: DIRECT OBSERVATION
OF STAMPS AND PATTERNED INK. Kenneth Sharp, Gregory
Blackman and Anand Jagota, Central Research, DuPont Co.,
Wilmington, DE.

Microcontact printing is a straightforward and effective method for
generating surface patterns of micron or sub-micron lateral
dimensions. The fidelity of the ultimate pattern is a complex interplay of
mechanical behavior of the elastomeric stamp, fluid transfer between surfaces and the ability of the ink to selfassemble on the new surface. We present here experimental observations and modeling of
stemp deformation during precise external loads and visualization of initial surfaces by several high contrast analytical techniques. Stamp behavior was observed visually in an inverted microscope and load-displacement relationships used to determine onset of failure modes such as roof collapse and buckling of slender relief features as a function of stamp geometry. The load was applied with a glass sphere so as to minimize problems with alignment and to precisely determine contact area. The work of adhesion between the two contacting
surfaces was also determined. A "robotic stamper" fabricated from an
AFM can deliver ink under conditions of precise load and registration and can be used to examine dilute patterns from multiple prints following a single inking procedure. Surfaces inked with varying
deposition combinations of Si and O showed a fundamental contrast by scanning surface potential microscopy (SSPM). The same
area of the sample can then be examined using time-of-flight SIMS or
scanning Auger nano probe with no additional etching or sample
preparation. In this way the depth and resolution of chemistry and purity of the patterned monolayers can be evaluated. The effect of load on ink pattern quality can be quantitatively evaluated.

420
1:30 PM US 1/WT 1
MULTISCALE MODELING OF VOID GROWTH IN DUCTILE METALS. Robert E. Rudd, Eira T. Seppälä, James Belak, Lawrence Livermore National Laboratory, Livermore, CA, CNRS/INPG, Domaine Universitaire, Grenoble, FRANCE.
Void growth is an important microscopic process in the fracture of ductile metals. In particular, micromechanics models are commonly used to describe the development and evolution of void populations through a coarse-grained porosity, but detailed models of void growth with atomistic level specificity have not been available. As the first steps in a hierarchical approach to this modeling framework, we are working on the development of a model for void growth associated with dynamic fracture, we have developed atomistic and mesoscale models [1, 2] that describe the evolution of voids under an applied stress. In our simulations this tension arises from expansion at a constant strain rate for comparison with dynamic fracture experiments conducted at LLNL and elsewhere. The hierarchical approach in effect replaces the empirical constitutive relationships used in continuum modeling of void growth with classical interatomic force laws, and the elastic and plastic behavior of the metal is derived from the collective response of the atoms. In this talk we compare the evolution of the plastic zone surrounding a growing void for several different ductile metals, including both face-centered-cubic (FCC) and body-centered-cubic (BCC) transition metals. In particular, we consider the characteristic of the dislocation activity, and we contrast the details of the plastic response for several metals. The dislocation characterization and nucleation rules we used to inform a dislocation dynamics simulation in order to extend to larger length scales at lower strain rates.

2:15 PM US 4/WT 4
MEASUREMENTS OF SIZE SCALE EFFECTS IN LAYERED STRUCTURES. A. Anton, C. Anton, A. Ion, Iowa State Univ, Dept of Aerospace Engineering and Engineering Mechanics, Ames, IA.
A novel experimental configuration is devised to measure the evolution of the deformation field and the corresponding toughness evolution within soft metallic films constrained by hard layers. The experimental configuration provides pure shear state within the constrained film. The multi-scale system utilized comprises an outer layer of Ta based solder, encapsulated within relatively hard copper shoulders. Different Ti/Leal composites are tested with grain size approaching the film thickness. The in-plane stress distribution within the film layer is measured by a microscopic digital image correlation system. The toughness evolution within such highly gradient deformation field is monitored qualitatively through a 2D surface scan with a non-indenter. The measurements showed a highly inhomogeneous deformation field within the film with discrete shear bands of concentrated strain. The localized shear bands showed long-range correlations of the order of 3-4 the grain size. A size-dependent macroscopic response of the layer thickness is obtained. However, the material behavior is characterized by orders of magnitude larger.

2:30 PM US 5/WT 7
TWO BRANCH UNIVERSAL BINDING ENERGY RELATIONSHIP FOR RELAXED SURFACES. Robin L. Hayes, Emily A.A. Jarvis, Emily A. Carter, University of California, Los Angeles, Department of Chemistry and Biochemistry, Los Angeles, CA.
In 1983, Rose, Smith and Ferrante proposed a Universal Binding Energy Relationship (UBER) to describe the binding between unrelated surfaces of many materials. Since then, UBER has been extensively used to represent correlation of crack surfaces in continuum models. Unfortunately, the traditional UBER model is incapable of capturing the substantial reduction in surface energies often caused by surface relaxation. We run a series of Density Functional Theory (DFT) calculations where we introduced a crack into a 3D periodic slab and allowed all the ionic to relax. The energies of relaxed surfaces can be separated into two regimes: elastic and cracked. In the elastic regime, the introduced crack leads to a uniformly expanded solid characterized by a chain of harmonic springs if the two surfaces are close enough for the electron density to bridge the gap. In the cracked regime, the traditional UBER functional form ceases to be correct and it is necessary to explicitly consider the interaction between relaxed surfaces. Our calculations show that the UBER is a brittle ceramic whose surface ions relax inward by nearly 1 Å, while [1] for Al is a ductile metal whose surface ions relax slightly outward by 0.1 Å. Both materials are well described by our 2-branch model. A Taylor expansion of the traditional UBER reveals that both harmonic and anharmonic terms are needed to fit DFT energies that should be purely harmonic. This leads to an artificially high elastic constant which produces errors if the traditional UBER is extrapolated to larger systems. Hysteresis arises from the nearly constant interplanar separation required for crack healing compared to the system size-dependent elastic behavior encountered prior to crack formation.

3:15 PM US/6/WT 6
APPLICATION OF A MODIFIED JOGGED SCREW MODEL FOR CREEP OF TITANIUM ALLOYS AND TITANIUM ALUMINIDES. Subramanian Karkikeyan, Gopal B. Vavassour and Michael J. Mills, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH.
Stress exponents for creep in the range of five are typically associated with non-activation creep processes, and a strong tendency for subgrain formation. This presentation will demonstrate that there are several important alloy systems that have similar stress dependence, and yet lack this tendency for subgrain formation. Specifically, dislocations in the intermetallic compound TiAl and the hexagonal close packed α-phase of the commercial Ti alloy Ti-6242 tend to be homogeneously distributed with a tendency for alignment along screw orientation. In both alloy systems, the screw dislocations exhibit a large density of pinning points, which detailed transmission electron microscopy
investigation indicate that locations of all jogs. These observations suggest that the jogged-screw model for creep should be appropriate after subcritical nucleation for the precipitation of shear localization. A modified jogged-screw model has recently been developed as an alternative explanation for creep in these systems. The model parameters are all measurable from TEM experiments, and the model is shown to correctly predict the creep rate and stress response for both $\gamma$-TiAl. This model has also been extended to treat the case of the lamellar microstructures that are common in both $\gamma$-TiAl and Ti-6242 alloys systems. A physical explanation for the formation of substructures described in this model and the potential application of this modified model to other alloy systems is discussed.

3:45 PM US 7/W7.7
NON-STICK AND SCRATCH RESISTANCE SOL-GEIS COATING FOR ALUMINUM Lisa Y. L. Wu and S.K. Chung, Singapore Institute of Manufacturing Technology, SINGAPORE

PTFE coating has been used for aluminum molds for molding of polystyrene packaging materials. However, this coating does not meet the users' requirements on scratch resistance and durability. Sol-gel technology allows the formation of a ceramic-like material at a lower temperature, which provides higher hardness and better scratch resistance for improved durability. This paper describes a study on the synthesis of a PTFE/SOL-GEIS composite material. This coating material combines the desirable non-stick and low friction properties of PTFE filler with the high scratch resistance and durability of a silica-based, ceramic-filled sol-gel material. The influences of colloidal silica, PTFE, aluminum oxide and titanium oxide fillers on the coating's non-stick, friction, and scratch properties are investigated. This sol-gel coating is applied to grit-blasted aluminum plates by spraying. The type of solvent used in the coating solution plays an important role in non-stick and friction properties, as well as in layer build-up and crack formation. We have found the optimum combination of fillers and solvents, which gives the minimum crack-free coating thickness. From which, a greatly improved anti-stick resistant coating with non-stick and low friction properties equal to those of PTFE coatings was obtained. The scratch resistance is twice that of the PTPE coating. To further improve the scratch resistance, the grit blasting process was replaced by an electro-chemical surface treatment. This treatment leaves a porous aluminum oxide layer, which allows material to penetrate into regular micro-pores (130 nm), resulting in strong mechanical interlocking. The adhesion between coating and substrate has been improved significantly relative to the normal grit blasting treatment. With this adhesion enhancement, the chipping problem of sol-gel coating was solved and the scratch resistance was increased by 4 times.

FE-SEM/EDX, contact angle tester, scratch tester and a pin-on-disc tribometer are used in the evaluation of the coatings properties.

4:00 PM US 8/W7.8
STRUCTURAL EVOLUTION AND ACOUSTIC PHONON BEHAVIOR IN CRYSTALLINE Pe-LFATE LAMINATES, Matteo Perno, Carlo S. Casari, Andrea L. Busi, Marco G. Beghi, Roberto Piazza, Carlo E. Bottini - Dipartimento di Ingegneria Nucleare, Politecnico di Milano, ITALY.

The surface and bulk structural evolution of polytetrafluoroethylene crystalline polymer film is studied at a length scale of few hundreds nanometers by atomic force microscopy (AFM) and Brillouin light scattering. Controlling the sintering process we observed a transition from the original particle distribution towards a 'fibrous' structure characterized by extended crystalline regions embedded in a disordered matrix, which still retains features of the original particulate structure. This transition has led to an observed cross-over from localized acoustic excitations to propagating acoustic phonons related with the mesoscopic elastic properties. The comparison with numerical simulations of the Brillouin scattering cross section shows that the sintered films do not yet exhibit the dynamical properties of the equivalent compact elastic continuum. This is in agreement with previous observations of the original particulate structure after sintering, suggesting that film formation for crystalline polymers may be analogous to sintering of ceramic powders. Brillouin spectroscopy of the latter systems is often difficult due to signal weakness. The formation of films of crystalline polymers can therefore be exploited as a model system to study the rheological properties of granular and disordered media. New phenomenology is also accessible, which is also relevant for the understanding of the sintering process of ceramic powders.

4:15 PM US 9/W7.9
GENERALIZED QUASICONTINUUM: AN APPROACH TO ATMOSPHERIC CONTINUUM MODELING OF COMPLEX OXIDES, Anter El-Azziz, Harold Tremain, James Rustad, Fundamental Science Directorate, Pacific Northwest National Laboratory, Richland, WA.

A formalism of the quasicontinuum method suitable for atomistic-continuum modeling and nanoscale mechanics of oxide crystals with basis is presented. Multiple interacting quasistatic deformation gradients in an atom by basis of the individual quasicontinuum, one per sublattice, which overlap in the physical crystal space are used to model complex oxide crystals. The Cauchy-Born hypothesis, which connects atomic coordinates in distorted crystals to the imposed deformation gradient, is assumed to be valid for the individual quasicontinuum. Based on a Delauney triangulation of the crystal and associated interpolation functions, the Cauchy-Born hypothesis is used to derive self-consistent coarse graining of the atomic forces of individual sublattices. Composition of forces and energy, however, takes into account the interaction among atoms on all sublattices. The method thus can be viewed as a numerical implementation of the theory of linear elasticity of crystals with basis. In this presentation, we show predictions of the structure of hematite (Fe2O3) crystal with and without imposed crystal distortions and compare with lattice statics results. A shell-type interatomic potential is used which accounts for the polarization of oxygen ions. In this case, the atomic shells associated with every oxygen sublattice are treated as separate sublattices, which accounts for doubling of the oxide quasicontinuum. Applications of this generalized quasicontinuum method developed here to study problems of structure and nanoscale mechanics are also discussed.

4:30 PM US 10/W7.10
AEROSOL DEPOSITION METHOD (ADM) FOR NANO-CRYSTAL CERAMICS COATING WITHOUT FIRRING, Jun Akeido, Masamune Lebedev, Atsushi Ishi, Hisato Ogiso, Shinuki Nakata, Inst. of Mechanical Engineering, National Inst. of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

A novel method of ceramics coating based on a particle collision, named as aerosol deposition method (ADM), will be reported. Sub-micron ceramics particles were accelerated by gas flow in the nozzle up to velocity of combustion of needle fire by a gas feed. Needle is made of metal, and heat by high power of current in the needle thinning the substrates. During impingement and interaction with substrate, these particles formed thick (over 1 μm), dense, hard and transparent ceramics layers with high deposition ratio (2 - 30 μm/min). Depositions were fulfilled at room temperature. No additional procedure for solidifications is required. The results of fabrications, microstructure and mechanical properties of oxide (Al2O3, YSZ, PZT, etc.), non-oxide materials and some composites will be presented. Hardness of PTZ layer having about 450 - 550 HV, which is over that of bulk material. Hardness of Al2O3 layer formed at room temperature reaches 2000 HV, which was measured by nano-indentor system and is comparable with that of bulk material. The adhesion force between the layer and the substrate was over 30 MPa. The microstructures were investigated by XRD and TEM. Every layer has polycrystalline structure with nanometer order scale. Crystal systems of layers were same as those of starting powders. Reduction of crystallite size from sub-micron order (100 - 500 nm) to nanometer order (- 20 nm) was observed during collision of particles.

4:45 PM US 11/W7.11
SYNTHESIS OF POLYMER/ MESOPOROUS SILICA NANOCOMPOSITES WITH ENHANCED MECHANICAL PROPERTIES, Xiaoling Ji, Eric Hampsey, Qingyuan Hu, Donghui Wang, Byron McCaughey, Xume Li, Yunfeng Lu, Department of Chemical Engineering, Tulane University, New Orleans, LA, Weihe Zhou, Advanced Materials Institute, University of New Orleans, New Orleans, LA.

Organic/inorganic nanocomposites often show unique properties due to the synergies of both components. Here we report the synthesis and enhanced mechanical properties of poly-[3-trimethoxysilyl]propyl methacrylate]-mesoporous silica nanocomposites. The synthesis approach involves infiltration and subsequent polymerization of the monomer [3-trimethoxysilyl]propyl methacrylate within mesoporous silica particles that are prepared using a aerosol-assisted surfactant-assembly process. Compared with poly-[3-trimethoxysilyl]propyl methacrylate polymer, as synthesized nanocomposites show a small decrease in tensile strain but significantly improved tensile strength, modulus, toughness, and thermal stability. Results from scanning electron microscopy (SEM) and other characteristic suggest that entanglement of the molecular chains formed within the mesoporous channels with those in the bulk polymer may contribute to the improved mechanical properties. Since conventional polymer/inorganic composites prepared using dense silica particles as fillers often result in an improved modulus but decreased toughness, this new approach provides a unique route to fabricate nanocomposites with both reinforcement and toughening.
residual stresses on debonding with particular attention to the relationship between the stress state in both ductile and elastic layers and the residual microcrack defect energy. It is shown that residual thin-film stresses can alter plasticity in the ductile layer and significantly influence the macroscopic fracture. It should be noted that the change in fracture resistance is not a result of modification of the debond driving energy, but rather stems from alteration of the yielding process in the ductile layer due to the superposition of the crack tip fields and the local residual layer stress. This superposition significantly alters the onset of yielding which in turn affects the final size and shape of plasticity in the ductile layer. Implications for the fracture resistance of nanometer scale device structures is discussed.

9:30 AM U9.4

ATOMISTIC SIMULATION OF FLOW STRESS AND DISLOCATION INTERFACE INTERACTION IN THIN METAL FILMS. Ya-Lin Shen and Bie S. Ege, Univ. of New Mexico, Dept. of Mechanical Engineering, Albuquerque, NM

A significant part of the strength of thin metallic films attached to a stiff substrate is derived from the interface constraint. This constraint is manifested by the high flow stress that can be carried by films on a substrate compared to the case of free-standing films. The substrate effect is typically removed from the energy approach involving the formation of misfit dislocations at the film/substrate interface. However, there is a general lack of experimental evidence of misfit dislocations in recent electron microscopy examinations of polycrystalline aluminum and copper films. In this study we invoke atomistic modeling to provide a mechanism for calculating the substrate effect for the substrate constraint in thin-film strength. Molecular statics simulations were carried out using the pair potential model for copper. The tensile stress-strain response is modeled for the free-standing and substrate-bonded films. It is concluded that the Schmid stress criterion is applicable in the stretched free-standing film, inducing slip steps at both surfaces of the film. The existence of an interface with the substrate constrains the dislocation motion in the film and restricts the slip steps to only the free surface. The propensity of film plasticity is dictated by the capability of atoms to slide along the interface. The higher flow stress in the substrate-constrained film, compared to the free-standing film, can be correlated with the atomic dislocation activities obtained from the simulation.

9:45 AM U9.5

THE EFFECTS OF GRAIN SIZE AND DISLOCATION SOURCE DENSITY ON THE STRENGTHENING BEHAVIOR OF POLYCRYSTALS. S.B. Biner and J.R. Morris, Metal and Ceramic Sciences, Ames Laboratory (USDOE), Iowa State University, Ames, IA.

In this study, the evolution of the flow stress for grain sizes ranging from about 11 to 0.5 μm under shear deformation was examined using two dimensional discrete dislocation dynamics. The grain boundaries were assumed to be both the only source for nucleation of the dislocations and also the only obstacles to the dislocation motion. The analyses were confined to a single slip system within each grain with varying orientations relative to the slip system of neighboring grains. The simulations were carried out for two sets of system sizes. In the first set of simulations the grain morphology was kept constant and the simulation unit cell size varied from 25x25 to 2.5x2.5 μm. In the second set of simulations the simulation unit cell size was kept at 25x25 μm and the grain size was varied. For the grain size range considered, an inverse relationship between the grain size and 0.2% offset flow stress in the form of Hall-Petch relationship [σ] = K/√d was observed, although there is some uncertainty in the exponent. The results of the study were performed for the United States Department of Energy by Iowa State University under contract W-7405Eng-82. This research was supported by the Director of Energy Research, Office of Basic Sciences.

10:30 AM U9.6

PREDICTING THE MORPHOLOGY AND MECHANICAL PROPERTIES OF DIBLOCK /NANOROD COMPOSITES. Zhenyu Shou, Gihan A. Butxon and A excellent, Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA.

We couple a morphological study of a rod filled diblock copolymer with a micromechanical simulation to determine how the spatial distribution of the rods and the copolymer domains affects the mechanical behavior of the nanocomposite. The morphological studies are conducted through a hybrid approach that couples self consistent field theory (SCF) for the block copolymers with density function theory (DFT) for the rods. Through these SCF/DFT calculations, we obtain the equilibrium morphology for the self assembled diblock/rod
mixture. The output of the SCF/DFT model serves as the input to the Lattice Spring Model (LSM), which consists of a three-dimensional network of springs. In particular, the location of the different phases is mapped onto the LSM lattice and the appropriate force constants are assigned to the LSM sites. A stress is applied to the LSM lattice and we calculate the elastic response of the material. We find that the local stress and strain fields are highly dependent on the properties of the constituents and morphology of the system. By integrating the morphological and mechanical models, we can establish how choices made in the components affect the ultimate performance of the material.


A generic polymer-based nanocomposite in which the polymer matrix is filled with spherical nanoparticles is analyzed. Monte Carlo simulations are performed to determine the polymer chain conformations and dynamics in the vicinity of the curved interface with the filler. The presence of the filler perturbs the polymer generating an “interaction zone” (IZ). The thickness of the IZ depends on the quantity being considered, for example, the IZ is one bond thick if one considers the polymer structure on the bond scale, about 2 gyration radii thick if the polymer structure on the chain scale is discussed, and is significantly thicker if one discusses chain dynamics. When the IZ size decreases constant fraction volume fraction, the inter-filler distance decreases such that the whole polymer matrix is perturbed (IZ). Continuum models for the elasticity and viscoelasticity of the composite are derived based on the polymer structure in the IZ determined from atomistic simulations. The continuum models are then used to homogenize the composite on larger scales.

11:00 AM U9.8 THE BEHAVIOR OF NANOPARTICLE CHAIN AGGREGATES UNDER STRAIN. A MOLECULAR DYNAMICS APPROACH. Ashkan S. Dula, Sheldon K. Friedlander, Dept of Chemical Engineering, University of California in Los Angeles, Los Angeles, CA.

Nanoparticle chain aggregates serve as reinforcing fillers that are combined with molecular polymers to produce nano-composite materials, e.g., carbon black in rubber. The reinforcing mechanism due to the incorporation of nanoparticle aggregates is not well understood. Molecular dynamics computer simulations are employed to investigate the behavior of nanoparticle chain aggregates under strain. The interaction potential used is that of Cu obtained with the embedded atom method. Cu was selected as a test material because reliable forms of the interaction potential are available. Single crystal Cu nanoparticles are placed in contact in various configurations including linear and kinked, and the structures are initially relaxed with molecular dynamics and/or Monte Carlo steps to establish an initial state. We observe plastic deformation during the sintering process for very small particles (3nm in diameter) at temperatures as low as 300K. The relaxed configurations are then strained to the breaking point at high strain rates (in the order of 1m/s), while the stress components are monitored. We identify mechanisms of strain accommodation such as interface sliding and dislocation gliding on the normal slip system of fcc Cu from the nanoparticle interface to the surface. The nanoparticle array configuration determines the dominant mechanism for plastic deformation.

11:15 AM U9.9 MECHANICS OF COMPRESSIVE STRESS EVOLUTION DURING THIN FILM GROWTH: PR. Gauvin, E. Chason, L.B. Freund, Division of Engineering, Brown University, Providence, RI.

Based on recent in-situ experiments, Chason et al. [1] proposed that the evolution of compressive stress during thin film growth is due to the formation in surface chemical potential in the presence of growth flux and the consequent exchange of adatoms between the free surface and the grain boundaries. Based on this hypothesis, we propose a model for grain boundary stress evolution during thin film growth. The calculations are carried out by solving the periodic wedge problem of Gao et al. [2], modified to account for growth flux. The adatom flux between the grain boundary and the free surface is assumed to be proportional to the difference in chemical potential between the two. These calculations successfully explain a wide range of experimental results, including the development of compressive stress during room temperature growth, effect of growth rate on the kinetics of compressive stress evolution and the continued tensile stress generation during low temperature growth. [1] Chason et al. (2002), Phys. Rev. Lett. 88(15), [2] Gao et al. (1999), Acta. Mater. 47(10), p. 385.